Box # G-4-3-17

ChemRisk/Shonka Research Associates, Inc., Document Request Form *

(This section to be completed by subcontractor requesting document)

J. Lamb / 1034A

Requestor — Document Center (is requested to provide the following document)

Date of request 9/14/95 — Expected receipt of document 10/14/95

Document number ~~[illegible]~~ none — Date of document ~~[illegible]~~ Fall 1969

Title and author (if document is unnumbered)

The Chromate Problem Fall 1969 [See Reverse for additional Info on this Pkg]

=> Please copy the entire folder

(This section to be completed by Document Center) cc: Steve Wiley *

Date request received —

Date submitted to ADC 10/18/95

Date submitted to HSA Coordinator —

(This section to be completed by HSA Coordinator)

Date submitted to CICO 10/18/95

Date received from CICO 10/19/95

Date submitted to ChemRisk/Shonka and DOE 10/23/95

1617

(This section to be completed by ChemRisk/Shonka Research Associates, Inc.)

Date document received

Signature

* 1 letter — Case to H D Hickman, 8/13/74, The Abatement of Chromate from New Hope Pond, Oak Ridge, Y-12 Plant — ~~Jen~~ Requires your release (attached) 10/18/95

Chromate Problem Fall 1969

This pkg was seperated as follows:

1) Portion sent to Y-12 for release

2) Portion sent to DOE-ORO (Joseph) for release

3) Portion sent to DOE-ORO (Rothrock) to obtain approval from other Companies to release

4) Misc K-25 Correspondence that has been approved for release

5) Documents that are being released "Limited" to ChemRisk only because of (A) procedure and (B) OUO document – these 2 documents are not being made ~~publicly~~ available and are being issued to ChemRisk and their subcontractors only.

Herb, We are keeping abreast of the various efforts on water treatment. Bill McCulla has been following the electro-chemical process for chromate removal from blowdown. Peterson, Patton, Shapiro, Vance, Pashley's people all keep in touch on an informal basis. As we've discussed its the high temperatures that make us reluctant to switch from chromates for our main water systems

1617

INTERNAL CORRESPONDENCE

NUCLEAR DIVISION POST OFFICE BOX P, OAK RIDGE, TENNESSEE 37830

To (Name) H. E. Trammell

Division

Location

Date January 24, 1973

Originating Dept.

Answering letter date

Copy to

J. S. Dalton
G. R. Jasny
A. J. Legeay
F. S. Patton
C. H. Peterson
S. J. Senatore
P. R. Vanstrum
W. J. Wilcox, Jr.
R. A. Winkel
File (4)

Subject Alternate Treatments for Recirculating Water System

In response to Mr. Vanstrum's question about the possibility of reducing our cooling water temperature in order to get away from a chromate-based water treatment, we have reviewed this, along with several other ways that might be used to eliminate the chromates from the water.

In the late 1960's the Utilities Departments at all three plants were aware that the discharge of hexavalent chromate to surface streams might, under state and federal laws, be considered a pollutant and as such prohibited. Extensive development programs were carried out on the ion exchange recovery method at both Paducah and Portsmouth. Recently some experimental work has been carried out at Paducah and Portsmouth on the reduction-precipitation process for removing hexavalent chromium from blowdown streams.

The Utilities Department at ORGDP requested a water treatment company to make an evaluation of the possible solutions to the blowdown problem in 1965. The report presented the economics of several processes, all of which resulted in higher operating costs.

It was believed that some provision should be made in the CUP Scoping Studies for resolution of the potential blowdown problem. As a result of this re-evaluation, the blowdown softening and recycle process was developed by C. C. Fowlkes and B. R. Webb of ORGDP's Utilities Department. The process is the simplest and most economic solution to the problem of chromate discharge to surface waters via cooling tower blowdown presently available. Several reports have been published on this method, the latest of which is "Softening of Cooling Tower Blowdown Water for Reuse," K-P-4023 by C. C. Fowlkes.

Therefore, the technology for the prevention of blowdown discharge of hexavalent chromium to surface waters has been developed at ORGDP. This has resulted in an overall reduction of approximately one order

1617

Prepared by Union Carbide Corporation-Nuclear Division, operating contractor for the U.S. Department of Energy under U.S. Government Contract No. W-7405-eng-26.

of magnitude in the total chromate discharged to the environment. However, there remains the potential problem of discharge through water droplets entrained in the vapor plumes from the towers. If this discharge is prohibited then it results in the elimination of chromate in the recirculation systems. This situation would necessitate an extensive testing program similar to that carried out in the late 1950's and 1960's at all three plants. We would make some effort to lower water temperatures but still be faced with major capital expenditures, increased fouling and off-stream time for continual condenser replacement. Table 1 (attached) from "Evaluation of Corrosion Inhibitors for Open Recirculating Water Systems," KY-455, 1964, by A. W. Gorline, gives a good indication of what we could expect. Our current operation with the chromate based treatment gives corrosion rates of about 0.1 mils per year on copper and < 0.5 mils per year on steel with no evidence of substantial pitting. The fouling on clean heat transfer surfaces is expected to be about 0.0005 hr ft^2 °F/Btu. With phosphate we would expect general corrosion rates of 1.0 mils per year on copper and 10.0 mils per year on steel. However, of more concern would be the pitting corrosion experienced on the copper condenser tubes which would result in increased failure rates and decrease cascade production. We would probably also see fouling on the order of 0.001 to 0.005 hr ft^2 °F/Btu.

In general, we are maintaining an unusually good water system for a chemical process plant. Fouling is virtually non-existant and the corrosion rate is negligible. Chromates appear to be the only widely accepted treatment for high temperature (over 120°F) service and are considered the best available for all conditions where minimal corrosion is important. Non-chromate water treatments are presently being inventigated for use in those portions of the ORGDP water system where temperatures are low and conditions are not so critical such as in K-25 and the fire water. The water conditioning industry is well aware of the problems associated with chromates and are actively working on developing and proving substitutes.

This is supposed to happen in next six months according to Charlie Faulkner of Utilities

As far as eliminating the chromates are concerned, one approach, of course, is to reduce the water temperature and go to some other treatment. However, since the same amount of heat must be removed, if the temperature rise is cut in half, then the water flow rate must double. To accommodate the extra water flow we would need additional towers and recirculating water lines, and probably some new and/or modified condensers. An alternative approach would be to add dry towers (air-cooled condensers) instead of the wet towers. We estimate that either of these schemes would involve capital expenditures of $10 to $20 million plus some additional operating expenses. If we went to wet towers, the cooler water vapor in the plume would be more susceptible to creating fog near the towers; this shouldn't be any problem but it is a factor to consider.

Another direct approach is to find a suitable water treatment for use at the present temperatures. Along this line, we've invited representatives from Water Services Incorporated of Knoxville, Tennessee to visit us and discuss a treatment they claim is environmentally acceptable and will perform at our temperatures. In addition, the Utilities Department is contacted almost weekly by other water treatment companies. These companies are also working on non-chromate treatments and we'll try to keep up with their developments.

There are also some indirect approaches that have been looked at, such as a heat pump system for heating and cooling buildings, and the power recovery concept. While these approaches would probably involve greater capital expenditures, they do have a potential for reducing overall costs.

We will have a much better idea of the magnitude of the problem when we get some results from the study we're just beginning on the environmental effects of cooling towers. In the meantime, we will keep in touch with the people at Y-12, ORNL and Paducah who are involved in this type of work and keep those involved informed of any pertinent developments.

B. F. Crump Jr.
B. F. Crump

C. C. Fowlkes
C. C. Fowlkes

G. J. Kidd
G. J. Kidd

J. M. Vance
J. M. Vance

BFC:CCF:GJK:JMV:jn

Attachment

KY-455

TABLE 1

CORROSION INHIBITOR HISTORY

Inhibitor	Chemical Constituent Balances in the RCW System	Test Duration Days	Corrosion Rates In Mils Per Year Copper	Steel
10-24-52				
Calgon	1 to 8 ppm Meta - PO_4 pH 7.6 to 8.1	-	No record.	No record.
Calgon	4 to 6 ppm Meta - PO_4 pH 6.5 to 6.9	46 copper 106 steel	1.0 Pitting Corrosion	10.0
Nalco 333	20-22 ppm Total - PO_4 1 ppm Sodium Ferricyanide pH 6.1 Ca Limit 350* ppm $CaCo_3$	40	2.2 Pitting Corrosion	5.2
Dianodic Orocol 181	20-22 ppm Total - PO_4 20-22 ppm CrO_4 pH 5.9 - 6.1 Ca Limit 300 ppm $CaCO_3$	80	0.27	0.52
Zinc Dianodic Orocol 175-Z Low CrO_4	10-13 ppm Total PO_4 10-12 ppm CrO_4 1.4 - 1.8 ppm Zn pH 5.9 to 6.1 Ca Limit 280-300 ppm $CaCO_3$	150	0.80	0.85
Zinc Dianodic Orocol 155-Z High CrO_4	10-13 ppm Total - PO_4 20-24 ppm CrO_4 1.4 - 1.8 ppm Zn pH 5.9 - 6.1 Ca Limit: 260-300 ppm $CaCO_3$ or 3.5 to 4.5 Cycles	160	0.15	0.35
Zinc Dianodic Orocol-TL Low PO_4	ppm Total PO_4 20-24 ppm CrO_4 ppm Zn pH 6.2 - 6.5 Ca Limit 450 ppm $CaCO_2$	172	0.12	0.15

*Approximate

1970 DEC 9 PM 2 37

Xy HET (sent 12/14)
file B54-1

UNION CARBIDE

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
P. O. BOX P, OAK RIDGE, TENNESSEE 37830

December 4, 1970

United States Atomic Energy Commission
Post Office Box E
Oak Ridge, Tennessee 37830

Attention: Mr. C. A. Keller, Director
Production Division

Gentlemen:

Chromate Usage and Disposal

The attached report gives some general background on water treatment at ORGDP and specifically covers various aspects of the use of chromate in water systems.

As indicated in the information presented, we know of no satisfactory substitutes for chromate as a corrosion inhibitor in relatively high temperature recirculating water systems.

A considerable effort has been expended in investigating and experimenting with various approaches directed toward removing chromates from the blowdown waters. As you know the problem was recently studied by an interplant committee consisting of personnel from ORGDP, Paducah, GAT, and Y-12, and a status report was issued*. Consideration of the several possibilities for amelioration of the problem indicated that both destruction-precipitation and ion exchange techniques would probably be successful should it be necessary to treat blowdown water. It was also concluded that choice of procedure might vary among the sites because of different conditions and restrictions.

---

* Dykstra, J., Pashley, J. H., Shapiro, T., ORGDP; Richardson, E. W., Paducah GDP; Kite, H. T., Y-12; Cooke, G. F., Seufzer, P. F., GAT; *Cooling Water Discharge Streams at Gaseous Diffusion Plants and Y-12*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, August 4, 1970, (K-GD-279).

A very promising technique which may solve the chromate disposal problem at ORGDP is to recycle the blowdown to the make-up water system and soften the mixture. This approach will avoid the discharge of chromate-laden water to receiving streams and will permit the recovery of chromates for reuse.

We hope this summary provides the information you desire.

Very truly yours,

R. G. Jordan

R. G. Jordan, Superintendent
Oak Ridge Gaseous Diffusion Plant

RGJ:ayb

Attachment

cc: Mr. J. M. Case
Mr. S. J. Cromer
Mr. R. F. Hibbs
Mr. W. J. Wilcox, Jr.
Mr. R. A. Winkel

WATER TREATMENT AT ORGDP

General Background

Initial operation of recirculating water systems at ORGDP required little treatment as return water temperatures were in the 100-110°F range. The total treatment consisted of maintaining 1-2 ppm polyphosphates at a pH of 7.7 with some intermittent chlorination. Steel corrosion rates were fair and due to the relatively high pH, copper corrosion rates were excellent.

The first indication of future difficulties at higher return water temperature was in the "C" loop (K-27/K-29). At return water temperatures of 120°F, serious process scaling occurred at the 7.7 pH. The pH was reduced to 6.7 by continuous sulfuric acid feed. This required more corrosion inhibition, resulting in the polyphosphate concentration increase to about 8 ppm. The corrosion rates were fairly high with these conditions.

The K-31 recirculating water was even hotter (130°F by the end of 1951 and 146°F by January 1954) and the high pH - low polyphosphate was discontinued after only a few months. The treatment was changed to that of "C" loop, but unsatisfactory high corrosion rates were experienced.

Before the K-33 recirculating water system was placed in service (March 18, 1954), it was decided that polyphosphate type treatment that could operate successfully at somewhat lower pH values to combat the scaling tendencies of the expected high return water temperature, would be necessary. The decision was made to use a polyphosphate with synergistic-action from a ferro-cyanide additive, at a recirculating water pH of 6.2-6.4. Fortunately, this treatment was discontinued on June 11, 1954 when the copper content had risen to 1 ppm (equivalent to 100 lbs of soluble copper in this system). Both steel and copper corrosion test nipples showed very high corrosion rates and it was decided that this treatment was operated at too low a pH value with no specific copper corrosion inhibitor (as chromates).

After an intermediate period with Calgon treatment, Betz Dianodic treatment with 20 ppm chromate and phosphate was started on October 12, 1955, and with some modifications has been in operation since that date. The steel and copper corrosion rates have been excellent. The successful Betz treatment was extended to other ORGDP recirculating cooling water systems.

Chromate Usage at ORGDP

Since inauguration of chromate treatment at ORGDP, the concentration level has been maintained almost continuously at the 20-ppm level for the high temperature systems (K-31 and K-33). For a short period a 10-ppm level of chromate and 20 ppm of phosphates was tried in the K-33 system, but inferior corrosion results prompted a quick return to the 20-ppm level. Other changes have been made in recirculating cooling water treatment, the most notable of which has been the reduction of phosphate concentration to 1-2 ppm level. This reduction has been accomplished by the addition of 2-ppm zinc. The lower temperature systems give satisfactory corrosion results at 10-ppm chromate level.

Our blowdown water has been reduced from over 5 million gallons per day to 1 million gallons. The major portion of this 1 million gallons per day that is removed from the systems is not needed for water treatment control but is "lost" due to nonreturn usage, primarily the K-1037/K-1100 buildings. It is planned to provide this facility with a separate cooling water system, thus eliminating the nonreturn usage.

Corrosion Test Results

The corrosion rates in systems containing chromates are compared with those using other treatments in the following table.

CORROSION RATES FOR DIFFERENT WATER TREATMENTS

	Corrosion Rate (mils/year)	
Treatment	Steel	Copper
Chromate	0.25*	0.555*
Nalco, synergist (K-33 startup)	40.0	5.0
Calgon, plain	1.7	0.2-1.5
Calgon, TG (130°F system)	1.5	0.1-0.5

* Four system average.

It should be noted that while a high corrosion rate is always objectionable, the average penetration in mils/year cannot necessarily be correlated to service life as pitting-type corrosion sometimes occurs.

Proposed Substitutes for Chromate-Type Recirculating Water Treatment

Although water treatment specialists offer nonchromate recirculating cooling water treatment, none have even suggested that their best nonchromate type treatment will give good results, economically and corrosion-wise with the ORGDP high return water temperature. Generally, their expected treatment costs are increased by a factor of five and upward with expected corrosion rates increased by the same factor.

A list of vendors who offer water treatment chemicals follows:

Betz Laboratories	Ionac Chemical Company
Calgon, Inc.	Nalco
Deaborn Chemical Company	Stauffer Chemical Company
Garratt-Callahan Company	Stein Hall & Company, Inc.

We, along with many others, are investigating and trying to follow new proposals for a substitute for chromate. It is our understanding that all water treatment specialists are working on this problem. We will continue to keep contact with chemical concerns offering new proposals. However, at this time, we are unaware of any acceptable substitute at high temperatures.

Future Plans

All the K-31 and K-33 blowdown requirements will be blended with raw Clinch River water and the mixture softened in the Accelators. In fact, for the last seven months all K-33 controlled blowdown (260 gpm) plus some (40 gpm) K-31 blowdown has been softened in this manner*. The results of this extended trial run have been encouraging. For the small remaining blowdown requirements from the low temperature systems, we plan to install a small reduction or recovery unit or pump back to the Accelators for softening, depending on the economics. It should be noted that our blending/softening operation recovers all the soluble chromates in the blowdown and they are available for reuse, reducing new chromate additions.

With present treatment available, the recommendation for ORGDP high temperature systems is the continued use of chromate treatment with chromate removal from any blowdown stream prior to discharge.

* Fowlkes, C. C., and Webb, B. R., *Experimental Softening of Recirculating Water Blowdown for Reuse*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, July 2, 1970.

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UNION CARBIDE

UNION CARBIDE CORPORATION

NUCLEAR DIVISION

P. O. BOX Y, OAK RIDGE, TENNESSEE 37830

Xy: HET
Our thanks to you. Know it wasn't an easy one + probably is not thru either!

August 24, 1970

United States Atomic Energy Commission
Post Office Box E
Oak Ridge, Tennessee

Attention: Mr. S. R. Sapirie, Manager
Oak Ridge Operations

Sent 8/27/

Gentlemen:

Cooling Water at Gaseous Diffusion Plants

Reference is made to your letter of September 26, 1969, asking that a study be made of the problems involved in cooling water discharge from our production plants, with particular emphasis on the problem of chromates. A joint UCND-GAT task force chaired by Mr. John H. Pashley of the ORGDP has completed the requested study of the three diffusion plants and of the Y-12 plant. This report was circulated in June in draft form for comments and is now being issued as report K-GD-279, *Cooling Water Discharge Streams at Gaseous Diffusion Plants and Y-12*, authored by Messrs. J. Dykstra, J. H. Pashley, and T. Shapiro of ORGDP; E. W. Richardson of Paducah GDP; H. T. Kite of Y-12; and G. F. Cooke and P. R. Seufzer of GAT. The report is dated August 4, 1970, and is being distributed separately.

Very truly yours,

R. F. Hibbs

R. F. Hibbs, President

RFH:WJW:rl

cc: Mr. J. M. Case
Mr. S. J. Cromer
Mr. R. G. Jordan
Mr. G. H. Reynolds
Mr. P. R. Vanstrum
Mr. W. J. Wilcox, Jr.
Mr. R. A. Winkel

1970 JUL 21 PM 2 50

UNION CARBIDE

INTERNAL CORRESPONDENCE

NUCLEAR DIVISION

POST OFFICE BOX P, OAK RIDGE, TENNESSEE 37830

To (Name)	Mr. W. J. Wilcox, Jr.	Date	July 17, 1970
Division			
Location	Building K-1004-A	Originating Dept.	Process Systems Development
		Answering letter date	
Copy to	Mr. H. E. Trammell File (NoRC)	Subject	Cooling Water Discharge Streams at Gaseous Diffusion Plants and Y-12

According to the discussions with Jerry Wing, who is gathering comments for Lenhard on the above, i.e., chromate report, they feel that the current version must be viewed as an interim report because it does not provide a cookbook solution for the problem. I agree; however, I feel that the report supplies the information requested by S. R. Sapirie's letter and set forth in your letter and Roger Hibbs' letter to Sapirie.

During the period the committee has been active, several progressive actions have been taken:

1. The K-25 water treatment group has implemented their blowdown resoftening work; i.e., chromate discharge avoidance by resoftening and reusing the flow which would be blown down to the streams.

2. Y-12 has looked hard at their problem and is planning tests with nonchromate inhibitors for their systems which involve lower water temperatures than at the diffusion plants.

3. Engineering activities including economic studies have been initiated at all plants.

4. Some additional test work has been performed at K-25 on continuous ion exchange with the result of verifying the Chem-Seps flow sheet, in general, but demonstrating that there may be some difficulty in assuring a 0.05 ppm chromium level without either a backup column or larger loading zone.

As I read your letter and that of Mr. Hibbs, it appears that the committee was appointed to prepare this report and that the issuance of the report would terminate its existence. I feel that I should point out both that the problem appears to be broadened because of several factors and that development of courses of action remains to be achieved.

Prepared by Union Carbide Corporation-Nuclear Division, operating contractor for the U.S. Department of Energy under U.S. Government Contract No. W-7405-eng-26.

The broadening of the problem has, to a large extent, been caused by the success of the ORGDP work on recycle softening. Both capital and operating costs presented by ORGDP make the approach look very attractive, and I'm sure that the AEC will feel this way because Wing has already commented thus. Both Paducah and Portsmouth have various objections, including difficulties in incorporation into their system due to the layout of their water systems and feelings that the operation at high solids content implied by the blowdown resoftening will cause additional operating and corrosion problems. Paducah furthermore has the concept of combining all liquid waste problems, such as fluorides, etc., with the water discharge; I don't know that this is desirable or inconsistent with some form of blowdown resoftening, but it does tend to broaden the problem. Thus, the various groups are beginning to look at the water problem from a source-to-sink standpoint including not only cooling water but other uses.

Getting action solutions to these problems is going to require:

1. Considerable engineering activity to get somewhat better than vague, conceptual designs and resultant cost estimates. This is going to require some source of funding.

2. Action on setting discharge criteria to allow some concentration of engineering and technical effort on at most a few solutions. The setting of criteria would seem to be a function of Lenhard's group.

3. Considerable expenditure of time on interactive study of problems at the gaseous diffusion sites if consistency of approach is to be assured.

The amount of time and effort required will be considerably more than has been consumed to date. It would be well to look at the structure of the groupings set up to handle these problems and the executive responsibilities assigned to get the work done. One might ask whether the failure of the two existing committees to come to a satisfactory conclusion on the chromate problem implies a failure of the existing configuration to meet the action requirements of the seventies. Perhaps assignment of responsibility at each plant to one division (Operations?) to meet requirements imposed by the AEC type committee would be desirable. A pollution engineer could be selected who would have the support from R&D, Works Lab, Legal (?), and Engineering Divisions and sufficient authority to expedite development and ratification of proposals, of course, assuming approval by management.

J. H. Pashley

J. H. Pashley

JHP:ga

Chromate Study

UNION CARBIDE

INTERNAL CORRESPONDENCE

NUCLEAR DIVISION

POST OFFICE BOX P, OAK RIDGE, TENNESSEE 37830

To (Name) Mr. P. R. Vanstrum

Division

Location 9704-2

Date December 8, 1969

Originating Dept.

Answering letter date

Copy to

Mr. R. C. Baker
Dr. H. A. Bernhardt
Mr. J. M. Case
Mr. G. F. Cooke, GAT
Mr. S. J. Cromer
Mr. J. Dykstra
Dr. J. M. Googin
Mr. A. P. Huber
Mr. R. G. Jordan
Mr. H. T. Kite
Mr. D. M. Lang
Mr. R. W. Levin
Mr. J. A. Parsons
Mr. J. H. Pashley
Mr. E. W. Richardson
Dr. P. R. Seufzer, GAT
Mr. T. Shapiro
Mr. I. G. Speas
Mr. H. E. Trammell
Mr. R. A. Winkel
Mr. E. J. Witkowski
Mr. W. J. Yaggi

Subject Cooling Water at Gaseous Diffusion Plants

You asked us to handle the AEC's request of September 26*, entitled "Cooling Water at Gaseous Diffusion Plants," which asked for a study of the chromate disposal problem in the CIP-CUP and for a report on the subject. This memo is to report the plans to handle this matter.

I have discussed the origin of the problem both with Leed and Lenhard. As you know, Leed is the chairman of the Technical Committee, Hazards of Process Gases in Diffusion Plants; and Lenhard is the chairman of the ORO Environmental Pollution Control Task Force. Neither of these groups—for various reasons—has been told to make the needed study on this chromate problem, and instead the AEC has written us this separate request.

I have asked a small group to undertake the specific task of making the needed study and preparing a report on this problem. In order to satisfy the AEC's interest in coordinating this study through the Pollution Control Task Force and to get input from the Hazards group as well, the committee will send draft copies of the report to members of

---

* Letter by Mr. S. R. Sapirie to Mr. R. F. Hibbs, "Cooling Water at Gaseous Diffusion Plants," September 26, 1969.

Prepared by Union Carbide Corporation-Nuclear Division, operating contractor for the U.S. Department of Energy under U.S. Government Contract No. W-7405-eng-26.

both the Pollution Control Task Force and to the Technical Hazards Committee for their comments. This should involve and collect the inputs of both of these groups and produce a useful report. The draft copy of the report should be in the hands of the reviewing committees by April 1, comments will be incorporated and the final report published prior to the AEC July 1 deadline.

I have talked several times to Roy Brown, asked what their plans were, and invited them to join us. I was recently informed that they have decided to join us and participate in the preparation of a single report (Sapirie wrote Reynolds a letter identical to the request to Hibbs asking for chromate study). The study group will be the following:

John Pashley, Chairman, K-25
Ted Shapiro, K-25
Joe Dykstra, K-25
Earl Richardson, Paducah
Harvey Kite, Y-12
Paul Seufzer, GAT
George Cooke, GAT.

Wm J Wilcox

Wm. J. Wilcox, Jr.

WJW:rl

1969 DEC 10 PM 2 28

UNION CARBIDE

UNION CARBIDE CORPORATION

NUCLEAR DIVISION

P. O. BOX Y, OAK RIDGE, TENNESSEE 37830

December 1, 1969

United States Atomic Energy Commission
Post Office Box E
Oak Ridge, Tennessee 37830

Attention: Mr. S. R. Sapirie, Manager
Oak Ridge Operations

Gentlemen:

Cooling Water at Gaseous Diffusion Plants

Your letter of September 26, 1969, requested that we give further consideration to the question of chromate releases from gaseous diffusion plants and consider our most reasonable alternatives in the event that more stringent requirements are placed on the amount of chromate which can be released to small surface streams.

In order to make these studies and to prepare the report requested, a small group is being assigned to this problem on a part-time basis. From discussions between Mr. Roy Brown of the Goodyear Atomic Corporation and Mr. W. J. Wilcox, Jr., it appears appropriate and desirable to work together in preparing this report. Representatives of the Paducah and Y-12 plants will also contribute to the study. It is planned that a draft of the study report for comments will be made available in late spring of 1970 to members both of the Oak Ridge Environmental Pollution Control Task Force and to members of the Technical Committee, Hazards of Process Gases in Diffusion Plants. Following incorporation of such comments as these two groups care to make, the report will be forwarded to you by your requested July 1970 deadline.

Very truly yours,

R. F. Hibbs, President

RFH:WJW:rl

cc: U.S.A.E.C. (4)	Mr. G. H. Reynolds
Mr. J. M. Case	Mr. P. R. Vanstrum
Mr. S. J. Cromer	Mr. W. J. Wilcox, Jr.
Mr. R. G. Jordan	Mr. R. A. Winkel

This document has been approved for release to the public by: Technical Information Officer, Oak Ridge K-25 Site, Date 10/18/95

Prepared by Union Carbide Corporation-Nuclear Division, operating contractor for the U.S. Department of Energy under U.S. Government Contract No. W-7405-eng-26.

1970 MAR 4 PM 4:15

UNION CARBIDE

INTERNAL CORRESPONDENCE

NUCLEAR DIVISION

POST OFFICE BOX P, OAK RIDGE, TENNESSEE 37830

To (Name)	Dr. K. A. Kraus	Date	February 27, 1970
Division	Oak Ridge National Laboratory		
Location	Building 4500-N	Originating Dept.	Materials Development
		Answering letter date	
Copy to	Mr. J. C. Barton	Subject	Chromate and Chromium Analyses in Water Samples

Mr. J. C. Barton
Dr. H. A. Bernhardt
Mr. J. Dykstra
Mr. T. Kwasnoski
Mr. J. H. Pashley
Mr. T. Shapiro
Mr. H. E. Trammell
Mr. W. J. Wilcox, Jr.
File

Basically two different methods are used for the determination of chromium in water samples by the Special Analysis Section under the direction of T. Kwasnoski. The choice of methods depends upon the chromium concentration. For discussion purposes, three chromium concentrations stated as chromate may be considered. These are as follows:

(1) Abvoe 30 ppm $CrO_4^=$ (chromate),

(2) 0.2 to 30 ppm $CrO_4^=$,

(3) Below 0.5 ppm $CrO_4^=$.

Samples having chromate concentrations above 30 ppm $CrO_4^=$ are diluted until the concentration is in the 0.2 to 30 ppm range and are then analyzed as for the second range by a colorimetric method employing a suitable spectrophotometer. The method determines only chromium in the hexavalent state and depends upon the formation of a red-colored complex in solution by reaction with diphenylcarbazide, $CO(N_2C_6H_7)_2$. The procedure employed, number 2.096.01.02, is attached. The range is 0 to 30 ppm $CrO_4^=$ and the limit of detection is 0.2 ppm. The precision at the 95% level of confidence is ±10% of the value.

Prepared by Union Carbide Corporation-Nuclear Division, operating contractor for the U.S. Department of Energy under U.S. Government Contract No. W-7405-eng-26.

If greater sensitivity is needed in the fractional ppm range an atomic absorption method is used. This method determines total chromium and does not distinguish between valence states. Below 0.2 ppm $CrO_4^{=}$ all samples are run by this method. The limit of detection without treatment to obtain an increase in the concentration is 0.05 ppm Cr. A 10:1 concentration by evaporation is practical and lowers the lower limit of detection to 0.005 ppm Cr (chromium). At a concentration level of 0.10 ppm Cr, the precision at the 95% level of confidence is ±0.02 ppm.

Both of these analyses are being run on a routine basis for recirculating cooling water and for raw makeup water respectively.

E. J. Barber
E. J. Barber

EJB:gu

Attachment

JHP

WJW, 12/8/69

GOODYEAR

Goodyear Atomic Corporation

P.O. Box 628
Pikeion, Ohio 45661

A SUBSIDIARY OF THE GOODYEAR TIRE & RUBBER COMPANY
ACTING UNDER U. S. ATOMIC ENERGY COMMISSION CONTRACT AT-(33-2)-1

TELEPHONE: PIKETON, OHIO AREA CODE 614-289-2511 TWX: 614-340-0900 TELEGRAMS: WUX-PIKETON, OHIO

December 2, 1969

GAT-501-69-40

U. S. Atomic Energy Commission
P. O. Box E
Oak Ridge, Tennessee 37830

Attention: Mr. S. R. Sapirie, Manager
Oak Ridge Operations

Subject: COOLING WATER AT GASEOUS DIFFUSION PLANTS

Gentlemen:

In response to your letter of September 26, 1969, requesting a study of chromate discharge reduction at the gaseous diffusion sites we will cooperate to the fullest extent. The problem of chromate release has been of concern to us and we have been engaged in several studies in this area including the recovery of chromates from the cooling water discharge. More attention has been directed to this approach because in addition to reduction of pollution of the receiving streams it provides an economic benefit by allowing reuse of the chromate recovered.

We have been invited by UCCND through Mr. W. G. Wilcox to join with them in th requested study and a joint UCCND-GAT task force has been formed to accomplish the study and report its findings. The GAT members of this task force will be Mr. G. F. Cooke, Supervisor of Utilities Operations, and Dr. P. R. Seufzer, Superintendent of the Development Laboratory. Mr. Cooke is also the GAT representative on the ORO Environmental Pollution Control Task Force.

If there is any further way that we can assist in this problem please let us know.

Yours very truly,

G. H. Reynolds
General Manager

This document has been approved for release to the public by: Henry H. Thomas, Technical Information Office, 19 Oct 95, Date

RWB:jr

cc: R. V. Anderson, PMA-AEC
L. B. Fuller, GAT
N. H. Hurt, GAT
R. M. Rutherford, GAT
C. D. Tabor, GAT
P. R. Vanstrum, Y-12
W. J. Wilcox, K-25

This document has been reviewed for classification and has been determined to be UNCLASSIFIED.
ADC Signature
10-19-95
Date

Post-it® Fax Note 7671

Date 10/18/95	# of pages ▸ 1
To Sheila Thornton	From Henry Thomas
Co./Dept.	Co.
Phone # 8 (615) 574-9595	Phone # 8 (614) 897-5791
Fax # 8/615/576-8191	Fax # 8 (614) 897-5734

UNION CARBIDE

INTERNAL CORRESPONDENCE

NUCLEAR DIVISION 69 NOV 26 PM 2 50

POST OFFICE BOX P, OAK RIDGE, TENNESSEE 37830

To (Name): Mr. P. R. Vanstrum

Division Location: 9704-2

Copy to

Date: November 26, 1969

Originating Dept.

Answering letter date

Subject: Cooling Water at Gaseous Diffusion Plants

You asked me to handle the AEC's request of September 26, entitled "Cooling Water at Gaseous Diffusion Plants," which asked that we study the chromate disposal proposal in the CIP-CUP and write a report on the subject. This memo is to report on plans to handle this matter.

I have discussed the origin of the problem both with Russ and Lenhard. As you know, Russ is the chairman of the Technical Committee, Hazards of Process Gases in Diffusion Plants, and Lenhard is the chairman of an ORO Pollution Control Task Force. Neither of these groups has been effective in mounting the needed study on this chromate problem for various reasons, and therefore they have written us this separate request.

I have made necessary arrangements for ~~My plan is to ask~~ a small group to undertake the specific task of preparing a study and report on this problem. In order to satisfy the AEC's interest in coordinating this study through the Pollution Control Task Force, ~~I propose that~~ the committee will send draft copies of the report to members of both the Pollution Control Task Force and to the Technical Hazards Committee for their comments. This should involve and collect the inputs of both of these groups and produce a useful report by their July deadline.

I have talked several times to Roy Brown and asked what their plans were and invited them to join us. I was informed November 25 that they have finally decided to join us and participate in the preparation of a single report (Sapirie wrote Reynolds a letter identical to the request to Hibbs asking for chromate study). The study group will be as follows:

John Pashley, Chairman, K-25
Ted Shapiro, K-25
Joe Dykstra, K-25
Earl Richardson, Paducah
Harvey Kite, Y-12
Paul Seufzer, GAT
George Cooke, GAT

Prepared by Union Carbide Corporation-Nuclear Division, operating contractor for the U.S. Department of Energy under U.S. Government Contract No. W-7405-eng-26.

I have drafted a letter to the AEC informing them of our overall plan and agreement with Goodyear which you may wish to transmit if you feel appropriate. Roy Brown says that Bud Reynolds is writing Sapirie telling him that they are participating.

Wm. J. Wilcox, Jr.

WJW:rl

Attachment (Draft)

will come in shortly

1969 OCT 2 PM 2 40

UNION CARBIDE **INTERNAL CORRESPONDENCE**

NUCLEAR DIVISION

POST OFFICE BOX P, OAK RIDGE, TENNESSEE 37830

To (Name) Mr. W. J. Wilcox, Jr.
Division
Location

Date October 1, 1969
Originating Dept.
Answering letter date

Copy to Mr. J. M. Case
Mr. R. G. Jordan
Mr. P. R. Vanstrum
Mr. R. A. Winkel

Subject

In reading the letter of September 26 from the AEC to Mr. Hibbs regarding cooling water at the gaseous diffusion plants, I thought the following information which was transmitted verbally to Mr. Hibbs several weeks ago on the question of chromate contamination might be useful.

A committee was set up some time ago to study pollution control problems in a number of AEC Production Division facilities. This committee consists of:

R. C. Baker - Paducah
J. Dykstra - K-25
I. G. Speas - Y-12
D. B. Jones - Goodyear
E. J. Witkowski - ORNL
J. B. Stevenson - National Lead
J. E. Lenhard - ORO, Research & Development
E. F. Newman - ORO, Engineering
George Rennick - ORO, Production

The following information was obtained from a discussion with Jack McLendon concerning the situation at the Y-12 Plant. Y-12 effluent is discharged into a lagoon near the East end of the plant. This is sampled at routine intervals and is composited on a monthly basis. The lagoon overflows into Poplar Creek. Hexavalent chromate content is from .12 to .25 averages about .18 ppm in the lagoon effluent.

According to Joe Dykstra, at the present time about 700,000 gallons of water per day blowdown from the cooling towers contains approximately 20 ppm. This is discharged through the barrier plant, where it is used for cooling purposes, into a holding pond. I believe that the discharge from the holding pond to Poplar Creek contains about 2 ppm of chromate. The Tennessee Health Department permits stream sampling and the discharge from Poplar Creek to the Clinch River

Prepared by Union Carbide Corporation-Nuclear Division, operating contractor for the U.S. Department of Energy under U.S. Government Contract No. W-7405-eng-26.

runs well under .05 ppm. As you know, Poplar Creek is not used as a source of potable water and carries, in addition to a great deal of surface runoff from the city of Oak Ridge, the effluent from the city's sewage disposal plant. We understand that the Tennessee Health Department is satisfied with the present operation.

Studies on power uprating indicate that cooling tower blowdown might be increased to as much as 4,000,000 gallons per day. $300,000 has therefore been included in our Long Range Plan (FY-72 General Plant Projects) for equipment to precipitate this chromium.

Si Bernstein has furnished this information regarding chromate discharge at Paducah. Cooling tower blowdown containing 20 ppm chromate is discharged into a surface stream which flows over government-owned lands to the Ohio River. TVA also discharges waste into this stream. The chromate content just before being diluted by the TVA stream runs about 2 ppm; after dilution it enters the Ohio River at 1 ppm chromate. It is believed that because of the very large dilution factor in the Ohio River that this discharge creates no health problem. We understand that Ohio has been appraised of this problem and has not yet reached a decision as to whether any corrective action is indicated. At the present time Paducah is experimenting with an ion exchange system for recovering chromate from cooling tower blowdown. $345,000 has been included in the FY-73 Long Range Plan for chromate recovery.

Sylvan Cromer

Sylvan Cromer

SC:bd

11/11/69 HFT:

INTERNAL CORRESPONDENCE

NUCLEAR DIVISION

POST OFFICE BOX P, OAK RIDGE, TENNESSEE 37830

To (Name) Dr. J. M. Googin w/attachment
Division
Location Y-12 Bldg. 9202

Date May 19, 1969

Originating Dept. General Engineering

Answering letter date

Subject Cascade Uprating Program
Process Cooling Water Systems
ESO M-35446-03

Copy to
Mr. C. C. Fowlkes w/attachment
Mr. R. B. Webb "
Mr. B. F. Crump "
Mr. J. Dykstra "
Mr. D. B. Janney "
Mr. R. L. Newton (3) "
Mr. J. A. Parsons "
Mr. T. Shapiro "
Mr. R. J. Thomas "
ESO File M-35446-03 RC "
BZimmerman Files (3) w/1 attachment

With reference to recent discussion with Mr. B. F. Crump of our Chemical Engineering Section, the following information is presented for your consideration.

It appears that the three plants which make up the diffusion complex will be faced with a pollution problem as to the rejection of cooling tower blow down containing approximately 20 ppm $CrO_4^{=}$ to surface waters. At the production level or power level anticipated at the end of the Cascade Uprating Program, each plant will be discharging approximately 4,000,000 gallons per day of cooling tower blowdown.

Of the several solutions to the problem, it appears that recovery of the chromate via semi-continuous ion exchange is attractive after a very cursory investigation.

The chemistry and static bed experience of the people at the Paducah Gaseous Diffusion Plant is presented in Report KY-548.

We have contacted the Chemical Separations Corporation for a preliminary design using their apparatus. Enclosed is a description of what they propose from a preliminary analysis. We would appreciate your comments and consultation as discussed over the phone on Friday May 16, 1969.

Our Utilities Department personnel, Mr. B. R. Webb and Mr. C. C. Fowlkes are interested in trying out a prototype unit if you think the system is applicable to our problem. We are sure that they would want to get together with you on discussing the operating problems and costs for semi-continuous ion exchange in general and this process in particular.

PROCESS

The system is based upon a patented process developed by the Nalco Chemical Company in which the cooling tower blowdown is acidified from about pH = 6.5 to 4.5 with sulfuric acid. The chromate is exchanged for the chloride ion in the loading section and the stripped acidified blowdown goes to a neutralization system before discharge to surface waters. The sodium hydroxide regenerant is evidently used to convert from an acid system to slightly basic in order for the following to occur:

$$R_2 - CrO_4 + 2\,Cl^- \rightarrow 2R\text{-}Cl + CrO_4^{=}$$ in the regeneration section.

Some conversion of the $CrO_4^{=}$ to $Cr_2O_7^{=}$ evidently also takes place.

The concentrated $Na_2Cr_2O_7$ and Na_2CrO_4 solution is recovered and sent back to the cooling tower system for recovery of its chromate value. The questions which have come to mind are:

1. The process design values such as NaCl, NaOH ratio and requirements, pH required resin type, etc., are based on Nalco's batch process experience. What changes would result from optimizing the system for the semi-continuous machine?

2. What should we use for operator and maintenance requirements for a large continuous system in order to do an economic comparison?

3. What is the anticipated resin usage characteristics of the machine, attrition, make-up, life, capacity variation with time, etc.?

4. What effects will other chemicals present in the blowdown have on the resin? In particular, we are concerned with the ~0.75 ppm free chlorine, ~20 to 30 ppm suspended solids and the ~600 ppm $SO_4^{=}$ present.

We hope to find a small unit available in the AEC complex. If no unit is available, then we will probably obtain one from Chemical Separations on a rental basis. There has been some discussion with both Nalco and Chemical Separations to the effect that if ORGDP was to buy and operate a 1 MGD (our present blowdown) demonstration plant the $10.50 royalty per year per GPM would be relinquished. However, we do not think we would want to commit in the order of $100,000 of capital money at this time without some experience with a smaller unit.

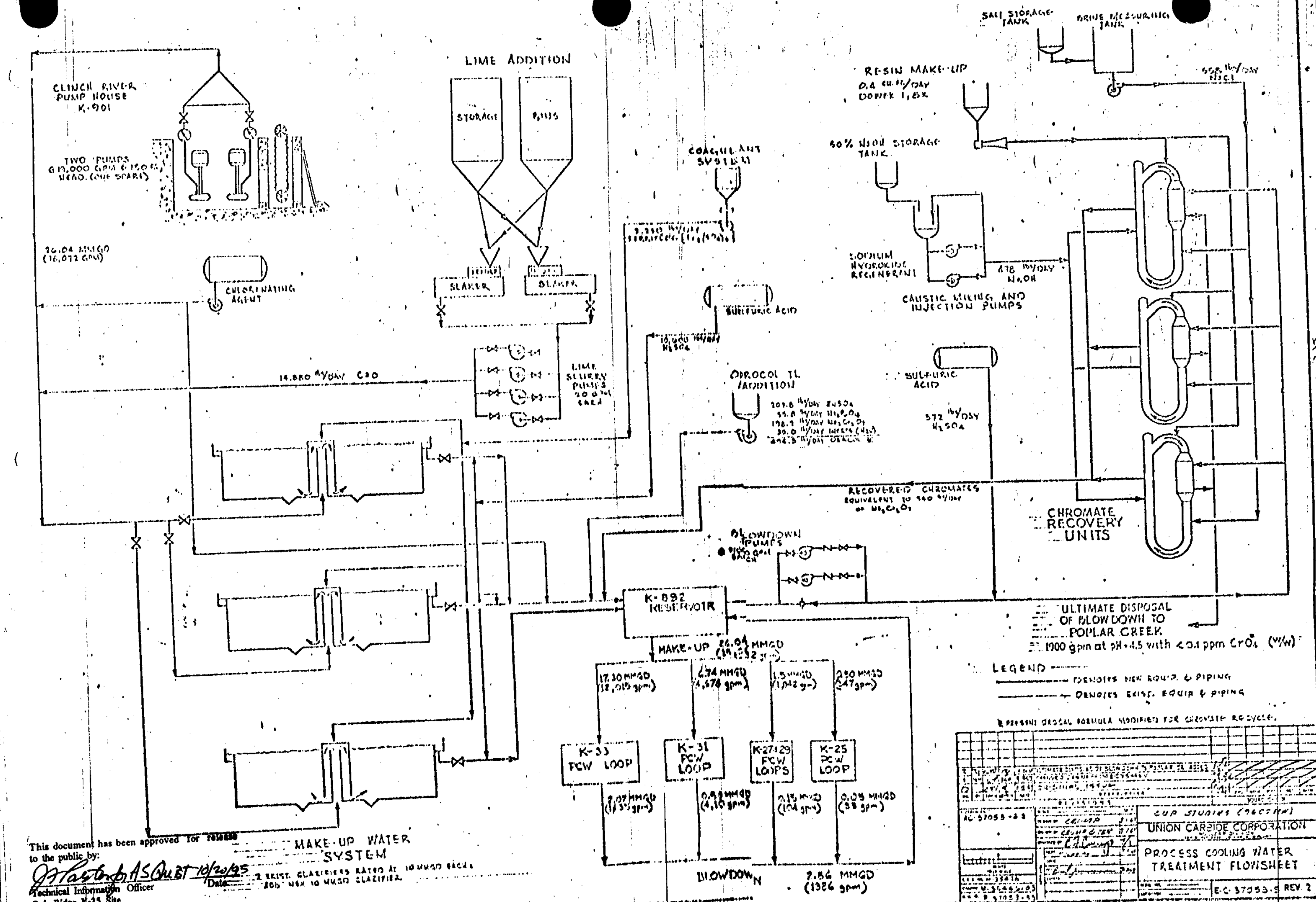
If the use of semi-continuous ion exchange does prove to be the best solution to thi problem, then we would have to consider it operating as a side stream calcium (or hardness) removal unit to eliminate blowdown entirely.

Your comments pertaining to these items will be appreciated.

Burl Zimmerman

Burl Zimmerman
General Engineering Department

BZ:BFC:mcs



This document has been approved for release to the public by:

J. Hartsock AS QULBT 10/20/95
Technical Information Officer Date
Oak Ridge K-25 Site

EXHIBIT III

	Make-up	Recirculating Loop *	Control Limits on Recirculating Loop
pH	7.0	6.6	6.4
	ppm	ppm	ppm
M Alkalinity (as $CaCO_3$)	9	8	
Total Hardness	56	368	
Calcium	28	196	
M-Phosphate (PO_4)	0.5	0.1	1.5 - 2.0
O-Phosphate (PO_4)	---	0.9	
Iron (Fe)	0.01	0.02	
Copper (Cu)	Neg.	Neg.	
Sulphate (SO_4)	36	374	
Turbidity (as SiO_2)	4	8	
Suspended Solids	Neg.	5	
Dissolved Solids	80	720	
Chromate (CrO_4)	3.6	16.0	20 - 22
Zinc (Zn)	0.45	1.95	2 - 3
Chlorides (Cl)	6	42	

* Based on trying to maintain 9 - 10 concentrations.

EXHIBIT V

Ferrous Sulfate Treatment System
(Based on Treating 1,000,000 gpd)

Reaction Tank	$11,500
Mixer	5,000
Ferrous Sulfate Feed System	4,000
Lime Feeding System	5,000
Flow Meter	1,000
pH Controller	2,500
Installation	5,000
Building	6,000
	$40,000
Alterations to Lagoon	20,000
	$60,000
Contingency	10,000
	$70,000

EXHIBIT V-A

Sulfur Dioxide Treatment System

Reduction Reaction Tank	$11,500
Mixer	5,000
Neutralization Tank	11,500
Mixer	5,000
Sulfur Dioxide Feed System	5,000
Sulfuric Acid Feed System	1,000
Lime Feed System	5,000
2 pH Controllers	5,000
1 ORP Controller	2,500
Installation	15,000
Building	12,000
	$78,500
Alterations to Lagoon	20,000
	$98,500
Contingency	16,500
	$115,000

EXHIBIT VI

Ion Exchange Recovery System
(Based on 1,000,000 gpd Blowdown Rate)

	20 ppm CrO_4	6 ppm CrO_4
Pounds of CrO_4 Discharged/Day	167	50
Pounds of CrO_4 Discharged/Year (250 Operating Days)	41,800	12,500
Value of Purchased Chromate (at 21¢/Lb. CrO_4)	\$ 8,780	\$ 2,630
Regenerant Cost (at 3.5¢/Lb. CrO_4)	\$ 1,465	\$ 438
Net Savings/Year	\$ 7,315	\$ 2,192
Cost for Ferrous Sulfate Removal Method	\$19,150	\$ 5,740
Total Chemical Savings/Year	\$26,465	\$ 7,932
Equipment Cost for Ion Exchange	\$195,000	\$195,000
Equipment Cost for Ferrous Sulfate	70,000	70,000
Increase in Equipment Cost	\$125,000	\$125,000
Amortization Period	4.7 years	15.8 years

KY-548
WASTE CHROMATE
RECOVERY BY
ION EXCHANGE

E.W. RICHARDSON
E.D. STOBBE
S. BERSTEIN

U.C.C.
N.D.
PADUCAH, KENTUCKY

1. Zimmerman, B., *Cascade Uprating Program Process Cooling Water Systems ESO-M-25446-03*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, May 19, 1969

2. Chopra, R. A., Letter to B. F. Crump, Chemical Separations Corporation, Oak Ridge, Tennessee, June 6, 1969

3. *Proposal for Chem-Seps Continuous Countercurrent Ion Exchange Pilot Plant Contactor for Union Carbide Corporation, Nuclear Division, Oak Ridge, Tennessee*, Chemical Separations Corporation, June 6, 1969 (Job No. 1589.

4. UCC Drawing entitled "Process Cooling Water Treatment Flow Sheet", July 2, 1969 (E-C-37053-S, Rev. 2)

5. Kelly, B. J.,"Removing Chromates - A Comparison of Ion Exchange and Reduction Processes for Removing Chromates from Cooling Tower Blowdown," Industrial Water Engineering, Chicago, Illinois, September 1968 (Nalco Reprint No. 174).

5. Hesler, J. C., Puckorius, P. R., and Farnsworth, N. B., "Recovery and Reuse of Chromates from Cooling Tower Blowdown", Proceedings, International Water Conference, Engineers Society of Western Pensylvania, Pittsburgh, September 28-30, 1964 (Nalco Reprint No. 150).

7. Hesler, J. C., and Oberhofer, A. W., "Recovery and Reuse of Chromates in Cooling Tower Discharge by Ion Exchange," Presented at Cooling Water Symposium, 20th Annual NACE Conference, Chicago, Illinois, March 9-13, 1964 (Nalco Reprint No. 130).

8. "Removal of Chromate from Cooling Tower Blowdown", Betz Laboratories, Inc., Philadalphia, Pennsylvania.

9. Paulson, E. G., Recommended Treatment Facilities for Cooling Tower Blowdown for Union Carbide Corporation, Nuclear Division, Oak Ridge, Tennessee, Hall Laboratories Division, Calgon Corporation, Pittsburgh, Pennsylvania, August 17, 1966 (Report No. C-483).

10. Richardson, E. W., Stobbe, E. D., and Bernstein, S., Waste Chromate Recovery by Ion Exchange, Union Carbide Corporation, Nuclear Division, Paducah Gaseous Diffusion Plant (K-Y-548).

Box # G-4-3-17

ChemRisk/Shonka Research Associates, Inc., Document Request Form *

(This section to be completed by subcontractor requesting document)

J. Lamb / 1034A

Requestor — Document Center (is requested to provide the following document)

Date of request 9/14/95 Expected receipt of document 10/14/95

Document number ~~[illegible]~~ none Date of document ~~[illegible]~~ Fall 1969

Title and author (if document is unnumbered)

The Chromate Problem Fall 1969 [See Reverse for Additional Info on this Pkg]

=> Please copy the entire folder

(This section to be completed by Document Center) cc: Steve Wiley *

Date request received —

Date submitted to ADC 10/18/95

Date submitted to HSA Coordinator —

(This section to be completed by HSA Coordinator)

Date submitted to CICO 10/18/95

Date received from CICO 10/19/95

Date submitted to ChemRisk/Shonka and DOE ~~10/23/95~~ 11/2/95

(This section to be completed by ChemRisk/Shonka Research Associates, Inc.)

Date document received

Signature

* 1 letter — Case to H D Hickman, 8/13/[illegible] The Abatement of Chromate from New Hope Pond, Oak Ridge, Y-12 Plant — ~~[illegible]~~ Requires your release (attached) 10/18/9[illegible]

1617

Chromate Problem Fall 1969

This pkg was separated as follows:

1) Portion sent to Y-12 for release

2) Portion sent to DOE-ORO (Joseph) for release

3) Portion sent to DOE-ORO (Rothrock) to obtain approval from other Companies to release

4) Misc K-25 Correspondence that has been approved for release

5) Documents that are being released "Limited" to ChemRisk only because of (A) procedure and (B) OUO document - these 2 documents are not ~~being~~ made ~~publicly~~ available and are being issued to ChemRisk and their subcontractors only.

JUL 24 PM 3 06

1617

UNITED STATES
ATOMIC ENERGY COMMISSION

OAK RIDGE OPERATIONS
P.O. BOX E
OAK RIDGE, TENNESSEE 37830

July 20, 1970

Approved for Release to the Public by:

Tim W. Joseph/sgt 10/30/9?
Timothy W. Joseph, Ph.D. Date
DOE Health Study Agreement COR

Union Carbide Corporation
Nuclear Division
Post Office Box P
Oak Ridge, Tennessee

Attention: Mr. J. H. Pashley

COOLING WATER DISCHARGE STREAMS AT GASEOUS DIFFUSION PLANTS AND Y-12

Gentlemen:

Reference is made to your multiple addressed letter dated June 16, 1970, requesting comments on the preliminary draft of the subject report.

The draft has been reviewed by representatives of the ORO Engineering, Production, and Safety Divisions as well as the Area Offices at Paducah and Portsmouth. Your committee has done an excellent job of surveying and documenting the problem and the draft appears acceptable in its present form as a status report with no major revisions required.

The draft correctly notes several areas that were deemed by the committee to be outside their purview but which have a significant bearing on the design of adequate chromium pollution abatement facilities. It is planned that ORO will resolve these questions and arrange for a meeting with you and your committee probably in the fall in order to provide sufficiently clear guidelines to enable your committee to develop a brief and specific final report which will hopefully include suggestions and alternatives for chromium pollution abatement at each of the four sites. These, in turn, could be used by the OR pollution control task force to recommend what, if any, corrective action is desirable at each installation based upon environmental consideration and standards.

We will be happy to work with you further in this matter.

Sincerely,

Joseph A. Lenhard

Joseph A. Lenhard, Director
Safety Division
Oak Ridge Operations

1617

OSH:JFW

cc: R. V. Anderson, PORT
B. N. Stiller, PAD
R. C. Armstrong, AMO, OR
C. A. Keller, Prod., OR
L. H. Jackson, Engr., OR
E. F. Newman, Engr., OR
G. Rennich, Prod., OR

This document has been reviewed for classification and has been determined to be UNCLASSIFIED.

ADC Signature

10-19-95

Date

1969 OCT 1 AM 10 50

cy: P. R. Vanstrum - 5, w. enc
H. G. MacPherson

UNITED STATES
ATOMIC ENERGY COMMISSION
OAK RIDGE OPERATIONS
P.O. BOX E
OAK RIDGE, TENNESSEE 37830

PRV: Please handle.
RFH 9/29/69

AREA CODE 615
TELEPHONE 483-8611

J. M. Case
S. J. Cromer
R. G. Jordan
W. J. Wilcox w/enclosure
R. A. Winkel

W. J. Wilcox - Please handle. We need to consider the Y-12 situation at the same time. PRV 9/30/69

September 26, 1969

Union Carbide Corporation
Nuclear Division
Post Office Box Y
Oak Ridge, Tennessee

Attention: Mr. Roger F. Hibbs, President

COOLING WATER AT GASEOUS DIFFUSION PLANTS

Gentlemen:

The question of chromate releases from gaseous diffusion plants has arisen quite frequently in the recent past during discussions with AEC Headquarters personnel concerning the cascade improvement and uprating programs, new plant additions for existing sites, and in consideration of Oak Ridge proposals for chromate removal.

Study of chromate discharges by members of our Oak Ridge Pollution Control Task Force has indicated that the matter deserves continuing attention. For your information, we have enclosed a copy of a brief report generated by our staff questioning the applicability of these current chromate limits, which are increasingly being applied to small surface streams. Copies of this report have been forwarded to our AEC Headquarters, soliciting their assistance in avoiding any unjustified requirements for effluent cleanup.

Pending the outcome of this effort, the increasingly widespread application of these chromate release limits to surface streams warrants further consideration of the situation at our gaseous diffusion plants. Specifically, we should consider our most reasonable alternatives should a limit of 0.05 PPM for chromates be placed on our first receiving stream. In previous discussions on this matter, it has been questioned whether chromates are the only reasonable corrosion inhibitor for use in gaseous diffusion plants and this might well be resolved. In general, it would be desirable to consider the situation existing when the plants are operating up to 9,200 Mw. Preliminary economic studies on this problem may also be desirable.

We plan that coordination of this study be carried out through our Environmental Pollution Control Task Force. However, since in-plant requirements on cooling water characteristics fall somewhat outside pollution control considerations, it is desirable that members of your technical development groups assist with the problem.

Your cooperation is requested in lending support to this effort as necessary to develop a summary report by July 1970.

Sincerely,

S. R. Sapirie
Manager
Oak Ridge Operations

OS:JAL

Enclosure:
Report

cc w/encl:
R. V. Anderson
B. N. Stiller

cc w/o encl:
R. C. Armstrong
C. W. Hill
L. H. Jackson
C. A. Keller
H. M. Roth
J. A. Lenhard

A REVIEW OF THE LIMITS FOR HEXAVALENT CHROMIUM IN SURFACE STREAMS

BY

DOROTHY A. ZEYEN

AND

JEROME F. WING

ORO

SAFETY DIVISION

September 8, 1969

INTRODUCTION AND SUMMARY

Chromate compounds are used quite extensively in various water treatment processes and, as a result, are often found in discharges of cooling waters from industrial facilities. As with many other metallic compounds, high concentration of chromates in liquid discharges present a hazard to aquatic life or to humans subsequently using these waters.

Many current standards and regulations quote a limit of 0.05 mg/l for chromates in drinking water. This limit is increasingly being applied to all parts of surface streams, and limits of 1.0 mg/l are being applied to discharges from facilities. While technology is available to reduce chromate concentration in liquid effluents, such processes have high initial cost and fairly high routine operating cost, particularly where large volumes of liquid effluents are involved and extremely low release limits must be met.

In attempting to justify the potential expenditure of sizable quantities of money for chromate removal at ORO facilities, a cursory study was made to ascertain the basis for and background of the 0.05 mg/l limit.

It was determined that current uses of the 0.05 mg/l limit for chromates are based upon extrapolations and, in some cases, misinterpretation of a small amount of questionable research data developed many years ago. Also, the few data relate to possible toxicity to a species of water flea and the 0.05 mg/l limit does not seem related to human toxicity. Further, the original references point out uncertainties in the data and warn against their adoption as limits. This report suggests that the 0.05 mg/l limit for chromates be questioned by responsible agencies, that appropriate research be sponsored for the establishment of more reliable limits for chromates, and that operating facilities not be pressed to make drastic process modifications pending the outcome of these studies.

DISCUSSION

Probable Origin of Current Limit

In the U. S. Public Health Service 1946 Drinking Water Standards, the limit of 0.05 mg/l for hexavalent chromium (Cr^{6}) was based on the lowest amount analytically determinable at the time it was established.[1] When this document was revised by the PHS in 1962 the chromium limit was continued since "a concentration of 0.05 mg/l is sufficiently low to cause no effect on health."[2] In addition, the PHS report states "At present, the level of chromate ion that can be tolerated by man for a lifetime without adverse effects on health is unknown." This 1962 publication references a report by the Ohio River Valley Water Sanitation Commission (ORSANCO) which indicated the chromate concentration toxic to Daphnia magna is 0.05 mg/l.

Since 1962 various states have used this figure as a guide in admitting chromium to surface streams especially where the use category is for a public water supply or aquatic life. A detailed review of the ORSANCO report[3] indicates that only five of the seventeen articles referenced dealt with the toxicity of chromium to Daphnia magna. Although the PHS lists 0.05 mg/l, the ORSANCO report lists the levels of toxicity to Daphnia magna as ranging from 0.06 mg/l CrO_3 to 0.29 mg/l for Na_2CrO_4.[4] The following is a review and brief appraisal of the five articles:

Ref. 483 - Private correspondence from Dr. W. H. Engels of Mercke & Co., Inc. This reference has not been located after considerable effort.

Ref. 45 - Grushko, Ya M. (1949). ORSANCO may have misused this article. Grushko makes no mention of the concentration or the limit of Cr for the survival of Daphnia. What he does state is that infusoria species were killed by a concentration of .05 mg/l in 7 days,[5] but he fails to mention which compound of Cr was used, how the experiments were carried out, or how many organisms were tested. The reference appears to be very general in nature and, as Grushko states, was written with the "objective of developing a multiple-basis method for health standards of permissible concentrations of toxic substances in water reservoirs,...."[6]

Ref. 30 - Anderson, B. G. (1944). This report concerns the experiments carried out by Anderson in which Daphnia was used as the test animal. He tested the toxicity of various substances in different concentrations, using Lake Erie water and an exposure time of 16 hours. Ten Daphnia were tested in each concentration, and the experiment was repeated three times. The immobilization of the Daphnia was used as the end point in determining toxicity thresholds.

Result:

CrO_3 $\ll$ 0.6 ppm toxic threshold[7]

$K_2Cr_2O_7$ $\ll$ 0.6 ppm

$\ll$ signifies value may be as low as 1/10 that given

Ref. 28 - Anderson, B. G. (1946). In 1946, Anderson repeated his experiment with Daphnia. Sixteen-hour exposure periods (1944) were found inadequate, for one-half of the animals had not reached the molting stage within 16 hours, and molting is considered a critical phase in the life of daphnids. Therefore, the time of exposure was increased to 48 hours. The experimental procedure was the same as that used in 1944.

Result:

Na_2CrO_4 $<$ 0.32 ppm toxic threshold[8]

$Na_2Cr_2O_7$ $\ll$ 0.31 ppm

$<$ signifies concentration might be about 9/10 that value given

$\ll$ signifies concentration might be as low as 1/2 the value given or less

Ref. 212 - Anderson, B. G. (1950). Anderson's experiments of the toxicity to Daphnia this time dealt only with the chlorides of various metals. His experimental procedure was identical to that employed before (1944, 1946) with one obvious exception: he now lengthened the exposure time to 64 hours. In the case of $CrCl_3$, Anderson noted that a grey precipitate was formed between the concentrations of .0003M and .0000027M, and that this may have played a part in immobilizing the daphnids through mechanical means.

Result:

$CrCl_3$ $\ll$ 3.6 ppm (.000023M) toxic threshold[9]

$\ll$ signifies concentration might be considerably lower than the value given

There are several important points to be made about these latter three articles:

1. All of Anderson's experiments on Daphnia were carried out prior to 1948.

2. In none of Anderson's experiments did the concentration-immobilization time curves for the chromium compounds ever reach their vertical asymptotes in the time allotted.

3. The values Anderson gives are not true threshold concentrations, but approximations based on extrapolation of the curves.

4. In the 1950 report, Anderson specifically states that "it is not my intention that the thresholds presented here should be set up as standards for admitting metal compounds into natural waters."[10]

5. The last two of Anderson's articles contain the remarks that "our present knowledge of the tolerances of aquatic animals to substances found in industrial wastes is fragmentary at best,"[11] and that "further research would be necessary to establish safe levels at which substances may be admitted to streams and lakes."[12]

Thus, review of the ORSANCO references indicates they are all somewhat inconclusive. ORSANCO's own recommendation was that further data is needed on chromium; however, a negative response was received to an informal inquiry asking if any additional work on chromium had been done since the 1950 report.

Current Use

Since 1962 various states have used 0.05 mg/l as a guide in admitting chromium to surface streams especially where the use category is for a public water supply or aquatic life. One of the most comprehensive state publications devoted exclusively to water quality criteria was published by California in 1963.[13] The California committee considered four different water use categories, and proposed different criteria for the quality of water in each category. The four categories of water involved were as follows:

a.	Domestic water supply	0.05 mg/l (Cr^3 or Cr^6)
b.	Stock and wildlife watering	5.0 mg/l
c.	Fish	1.0 mg/l
d.	Other aquatic life	0.05 mg/l

The committee felt that the concentrations given above would not interfere with the specified beneficial use of the water. The California committee also quoted ORSANCO on the toxicity of Cr to Daphnia; however, the figures are not in agreement: 0.016 ppm $Na_2Cr_2O_7$ given by the California committee[14] as opposed to the 0.31 ppm given in the ORSANCO report.[15] Other concentrations cited by the California committee as being toxic to Daphnia magna range from .05 ppm (misquote: Grushko 1949) to 0.7 ppm (Bringmann 1959).[16] The lower figures are the result of experimentation done prior to 1950, while more recent experimentation has yielded toxicity levels 10 to 14 times the present standard.

The National Technical Advisory Committee (NTAC) to the Secretary of the Interior proposed a method for establishing water quality criteria similar to that of California. The NTAC recommended specific water quality characteristics to serve five purposes: (1) recreation and esthetics; (2) public water supply; (3) fish, other aquatic life, and wildlife; (4) agricultural uses; and (5) industrial water supply.

In reviewing the affect of the heavy metals on fresh water organisms, the NTAC talks briefly about Cr^6. The Committee references a number of experiments dealing with various types of fish and algae, and oddly enough picks up the California figures (0.016 ppm - 0.7 ppm) for the toxicity of hexavalent chromium to Daphnia magna.[17] As the Federal Water Pollution Control Administration notes, one of the problems relating to water quality standards is the lack of adequate knowledge concerning many of the quality characteristics upon which criteria should be based. In this context, the NTAC made the following recommendation with regard to the level of chromium permissible in various types of water: "Data are too incomplete to do more than urge caution in the discharge of chromium."[18]

The Water Pollution Control Board for the State of Ohio recently adopted water quality criteria which require every surface stream in the Scioto River Basin (with minor exceptions) to meet the criteria for all uses by January 1, 1972.[19]. When the use category is for a public water supply, the 0.05 mg/l limit for Cr^6 applies at the point where water is withdrawn for treatment and distribution as a potable supply. In those locations where the use category is aquatic life, the limit for toxic substances is "not to exceed one-tenth of the 48-hour median tolerance limit, except that other limiting concentrations may be used in specific cases when justified on the basis of available evidence and approved by the appropriate regulatory agency."

The Ohio Water Pollution Control Board was contacted informally in an effort to determine the one-tenth median tolerance limit (TL_m) for hexavalent chromium, fluorides, nitrates, etc. The Ohio representative stated they had no such list and could recall only the TL_m for cyanide of 0.02 mg/l (which happens to be one-tenth the PHS drinking water limit). As for hexavalent chromium (Cr^6) the Ohio representative stated the TL_m would be about the same as or perhaps a little less than the PHS drinking water level of 0.05 mg/l. He added that "since the technology is available for removal of almost all the hexavalent chromium, why not do it?" In essence, it appears that the concentration of Cr^6 in all places in every river stream, or brook in the State of Ohio must not exceed the Public Health Service requirement of .05 mg/l.

Although Tennessee has not yet formally adopted applicable criteria for intrastate streams, it was learned their representatives are tentatively considering adoption of a Cr^6 limit of 1.0 mg/l in the effluent pipeline and 0.05 mg/l in the receiving stream.

Conclusions and Recommendations

It appears that the figure of .05 mg/l was intended solely as a standard for public drinking water supplies, and, as such, the figure should not be abritrarily applied as a criterion for all surface water. Besides noting that the present concentration of chromates occurring naturally in surface water is in the range of 0.0 - 2.3 mg/l[20] no specific recommendation is made by the Public Health Service for water other than that used for drinking purposes.

It is recommended that:

1. the 0.05 mg/l limit for Cr^6 in surface streams be questioned by responsible agencies,

2. appropriate research be initiated which would provide an adequate and scientific basis for determining the permissible levels of Cr^6 in surface streams,

3. operating facilities not be pressed to make drastic process modifications pending the outcome of these studies. This recognizes the fact that the Bureau of the Budget Circular A-81 in AEC Appendix 0510 requires Federal agencies to develop a phased and orderly plan to achieve compliance with Executive Order 11288 by July 1, 1972.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of the excellent staff of the Library, Oak Ridge Associated Universities for their untiring efforts in locating and providing copies of many of the references used herein and the assistance of Miss Martha W. Gerrard, ORNL, and Miss Margaret L. Pflueger, Division of Technical Information Extension, for translating the Russian article (Grushko).

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13. Water Quality Criteria, State of California, Second Edition, 1963.

14. Ibid, p. 165 (table).

15. Ohio River Valley Water Sanitation Committee; Subcommittee on Toxicities, Report #3, Section IV, 1950, Ref. #28.

16. Water Quality Criteria, State of California, Second Edition, 1963 p. 165 (table).

17. Report of the Committee on Water Quality Criteria, Federal Water Pollution Control Administration, April 1, 1968, Washington, D. C. p. 61.

18. Ibid, p. 61.

19. Water Pollution Control Board, Department of Health, Columbus, Ohio; "Water Quality Standards Adopted by the Board April 9, 1968. For the waters of the Scioto River Basin.

20. Public Health Service Drinking Water Standards; 1962, p. 37.

Box # G-4-3-17

ChemRisk/Shonka Research Associates, Inc., Document Request Form

(This section to be completed by subcontractor requesting document)

J. Lamb / 1034A

Requestor — Document Center (is requested to provide the following document)

Date of request 9/14/95 — Expected receipt of document 10/14/95

Document number ~~[illegible]~~ none — Date of document ~~[illegible]~~ Fall 1969

Title and author (if document is unnumbered)

The Chromate Problem Fall 1969 [See Reverse for additional info on this pkg]

=> Please copy the entire folder

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Date submitted to ChemRisk/Shonka and DOE ~~10/23/95~~ 10/31/95

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Date document received

Signature

1617

* 1 letter — Case to H D Hickman, 8/13/- The Abatement of Chromate from New Hope Pond, Oak Ridge, Y-12 Plant — ~~[illegible]~~ Requires your release (attached) 10/18/-

Chromate Problem Fall 1969

This pkg was separated as follows:

1) Portion sent to Y-12 for release

2) Portion sent to DOE-ORO (Joseph) for release

3) Portion sent to DOE-ORO (Rothrock) to obtain approval from other Companies to release

4) Misc K-25 correspondence that has been approved for release

5) Documents that are being released "Limited" to ChemRisk only because of (A) procedure and (B) OUO document - these 2 documents are not being made ~~publicly~~ available to ChemRisk and and are being issued to ChemRisk and their subcontractors only.

1617

CHEMICAL ANALYSES DEPT.
SPECIAL PROBLEMS SECTION

Date Dec. 4, 1967.

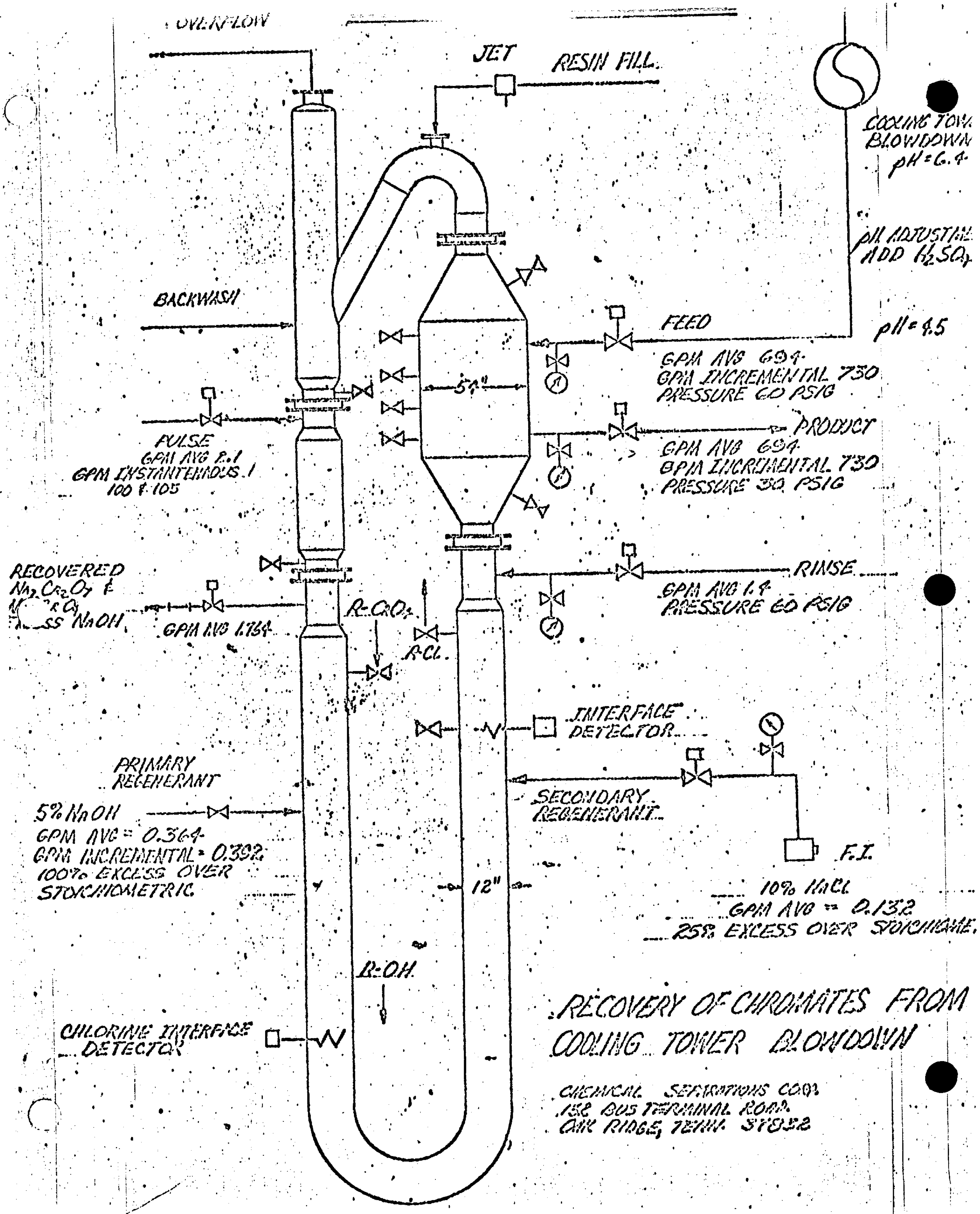
Sample / Test				Recirculating Loop Samples				
	CW-1	CW-7	Raw	Makeup	A&B	C	E	G
pH			7.3	4.7	6.4	6.5	6.1	6.3
"M" Alk. (as $CaCO_3$) ppm			45	2	9	10	11	12
Total Hardness "			70	88	242	480	510	510
Calcium " "			34	64	144	282	308	310
M-phosphate (as PO_4)"				.3	.2	.3	.2	.4
O-phosphate (as PO_4)"					.5	.9	1.0	.7
Iron (as Fe) "			.08	.06	.04	.04	.08	.05
Copper (as Cu) "			0	.02	.02	.04	.02	.04
Sulphate (as SO_4) "			22	64	240	528	572	570
Turbidity (as SiO_2) "			57	22	6	15	25	23
Suspended Solids "			49	37	4	8	21	20
Dissolved Solids "			150	140	500	1020	1040	1020
Chromates (as CrO_4)"				4.0	11.4	21.2	21.6	22.0
Zinc (as Zn) "			.05	.35	1.2	2.25	3.1	2.15
Chlorides (as Cl) "			5	8	41	78	76	80

Blowdown Water Analysis

Condensers North 6.4 pH
South 6.4 pH

Signed: J. R. [illegible]

1617



RECOVERY OF CHROMATES FROM COOLING TOWER BLOWDOWN

CHEMICAL SEPARATIONS CORP.
138 BUS TERMINAL ROAD
OAK RIDGE, TENN. 37832

5/14/69

UNION CARBIDE
NUCLEAR DIVISION

OPERATING COST

Basis: 1 MGD

			Per Day or Per M Gallons
A.	**Chemicals:**		
1.	H_2SO_4 for lowering of pH 200 lbs/Day @ 1.5¢/lb	=	\$ 3.00
2.	NaCl 220 lbs/day @ 1¢/lb	=	\$ 2.20
3.	NaOH 230 lbs/day @ 3¢/lb	=	\$ 6.90
4.	Resin 150 cu.ft. total inventory 3 year life, 365 working days/year	=	\$ 8.20
	Total Chemical Cost/M Gallons	=	\$20.00

Chemical Cost per lbs. of recovered $CrO_4 = \frac{20}{167}$ = \$0.12/lb of CrO_4

B.	Capital Cost for 4 MGD plant	=	\$420,000.00
C.1.	Royalty to NaCO - \$10.50 per year/GPM	=	\$7,291.66/year
2.	Royalty/M Gallons @ 365 working days	=	\$19.97
	Royalty/lb of CrO_4	=	\$0.1196
D.	Total Operating Cost/Day	=	\$39.97
E.	Cost of Recovery/lb	=	\$0.2393
F.	Credit for 167 $CrO_4^{=}$ at \$0.35/lb ?	=	\$58.45/day

Assume credit to diffusion plant for recovered chromate minus water treatment royalty is \$0.35 - \$.10 = \$.25/lb. $CrO_4^{=}$

Credit per MGD for 167 lbs ...... − \$41.73
Operating costs per MGD ...... + \$39.97
Capital @ CRF 0.13 ...... + 37.40

58.45
39.97
37.40
18.92

BETZ LABORATORIES, INC.

Betz Labs analysis

REMOVAL OF CHROMATE

FROM

COOLING TOWER BLOWDOWN

INTRODUCTION

Ever tightening State and regulatory body restrictions have resulted in the placing of stringent limits on the concentration of toxic compounds which may be discharged to water courses and waste treatment plants. Among the toxic materials which are receiving particular attention is chromium in both the hexavalent and trivalent forms. Since chromate is a fundamental and important constituent of many effective cooling tower corrosion inhibitor programs, it is especially important that, where required, the customer be appraised of the means of removing chromate from his cooling tower blowdown to render the resulting waste stream acceptable to receiving bodies. This discussion will deal with the several means of reducing and eliminating chromate from cooling tower blowdown, one of which might be implemented by the user in the event that he is forced to remove chrome from his cooling tower waste stream.

In general, the chemical removal of chromate from cooling tower discharge can be divided into two steps:

1) Reduction of chromate to trivalent chromium.
2) Precipitation of trivalent chromium as chromium hydroxide and its separation from the blowdown stream.

The reduction of hexavalent to trivalent chromium reduces the toxicity by a factor of 100[1], however, more and more State Health Departments

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[1] Reduction of Toxic Chromium Wastes with Sulfur Dioxide - "Chlorination Topics", Vol. 5, No. 4, April 1952.

are demanding practically complete removal of chromium to .05 ppm[1] which necessitates the removal of trivalent chromium as well. Therefore, the methods described below will encompass the complete removal of chromium from cooling tower blowdown streams.

CHEMISTRY OF CHROMATE REMOVAL

The most prevalent methods of removing chromate from aqueous streams employ the chemical reduction of hexavalent form to trivalent chromium followed by neutralization and precipitation of chromium hydroxide and its subsequent removal.

The reduction of chromate to trivalent chromium is accomplished readily at reduced pH. At higher pH the rate of reaction is drastically reduced and becomes impracticably slow much above a pH of 4.5 - 5.0. In most cases, the optimum pH will be controlled in the range of 2.0 - 3.0.

A variety of reducing agents are employed for the reduction of chromate. Most common, however, are the following:

1. Sulfur Dioxide
2. Sodium Bisulfite $3 Fe^{++} + Cr^{+6} \rightarrow 3Fe^{+3} + C$
3. Sodium Sulfite
4. Sodium Metabisulfite
5. Ferrous Sulfate
6. Hydrogen Sulfide (limited use as by-product waste)

Of these, sulfur dioxide, ferrous sulfate, and sodium metabisulfite are used most prevalently. Typical reactions are illustrated below along with theoretical stoichiometric quantities required. It should be realized that in actual

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[1] U.S. Public Health Service Drinking Water Standards.

practice significant excesses of these chemicals over the theoretical requirements are invariably necessary to accelerate the rate of reaction and overcome adverse side effects.

When sulfur dioxide is employed as a reducing agent, the dissolved oxygen content of the water being treated reacts with it and will be consumed forming sulfate. The consumption of sulfur dioxide by dissolved oxygen in the water being treated will be a significant portion of the sulfur dioxide required for the reduction of the chromate. In addition, excesses of sulfur dioxide are normally applied to insure rapid reaction rates.

$Cr^{+6} + 3e^{-1} \rightarrow Cr^{+3}$

1. $\overset{+6\,-6}{2CrO_3} + 3SO_2 \rightarrow \overset{+3}{Cr_2}\ \overset{-6}{(SO_4)_3}$

   1# 0.96# 1.96#

2. $4CrO_3 + 6NaHSO_3 + 3H_2SO_4 \rightarrow 3Na_2SO_4 + 2Cr_2(SO_4)_3 + 6H_2O$

   1# 1.56# 0.74#

3. $2CrO_3 + 3Na_2SO_3 + 3H_2SO_4 \rightarrow 3Na_2SO_4 + Cr_2(SO_4)_3 + 3H_2O$

   1# 1.89# 1.47#

4. $4CrO_3 + 3Na_2S_2O_5 + 3H_2SO_4 \rightarrow 3Na_2SO_4 + 2Cr_2(SO_4)_3 + 3H_2O$

   1.0# 1.43# 0.74#

5. $2CrO_3 + 6FeSO_4 \cdot 7H_2O + 6H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 48H_2O$

   1# 8.34#

All of the above reactions are carried out on the acid side, some necessitating the addition of an acid such as sulfuric to insure a rapid reaction rate and minimum quantities of reducing agent. All of the procedures convert hexavalent chromate to trivalent chromium and must therefore be followed by a supplementary step to remove trivalent chromium from solution. Most commonly, this is accomplished by elevating the pH of the waste stream to 8.0 - 9.0, thus producing the precipitate chromic hydroxide. Lime is most often utilized for this purpose because of its availability and low price, however, sodium hydroxide or any other available alkali may be preferred in smaller installations because of the greater ease of handling or immediate availability. The 'precipitation - reaction' is illustrated below:

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4$$

$$(1.11\# \quad Ca(OH)_2 \ / \ \#CrO_3)$$

Adequate time must be provided for the settling of the chromic hydroxide precipitate and its subsequent removal from solution. This hydroxide is relatively slow in settling and therefore, if it is to be separated from the waste liquid stream by gravity, a settler with about 2 hours residence time is normally required.

Table I summarizes the stoichiometric chemical requirements and the estimated costs for the destruction of chromate and precipitation of trivalent chromium by the several methods described above.

Again, it should be stressed that the presence of alkalinity, dissolved oxygen and several other constituents may result in the use of considerably more acid and reducing agent to effect the reduction than that indicated by the stoichiometric equivalents in Table I.

It is apparent from the comparison of destruction costs of the several alternatives that with the exception of ferrous sulfate they are all roughly comparable. Ferrous sulfate is one of the early chemicals used and is still applicable today for smaller systems or where improved settling rates are especially desirable. The ferric ion formed in the destruction reaction precipitates in the alkaline solution forming ferric hydroxide which serves as a coagulant to assist in bringing down the slow settling chromic hydroxide. Generally, ferrous sulfate would be supplemented by one of the other reducing agents in larger systems due to the chemical destruction cost savings possible.

BATCH VS. CONTINUOUS SYSTEM

The chemical destruction method for treating chromate bearing blowdown waters may be handled in either a 'batch' or 'continuous' system. The batch treatment system is generally applicable to smaller systems discharging up to 25 to 30 gpm and may involve tandem holding tanks for semi-continuous operation. One tank will be filling while the destruction process is being carried out in the other. Since the minimum recommended settling time following the precipitation of chromic hydroxide is 2 hours each of these batch holding tanks must be sized for about 3 to 4 hours capacity.

Figure I shows a typical batch destruction facility. In this case, common feeders providing sulfur dioxide, sulfuric acid and caustic are used alternately with each of the chromate waste holding tanks. The treatment is begun after a storage tank is filled with blowdown waste. The recirculating pump operates during the entire procedure providing the mixing energy for the waste and chemicals being added. In the initial step, the acid pump is operated to reduce the pH of the contents of the waste holding tank to between 2.0 and 3.0. For this purpose, a pH recorder-controller may be used although not absolutely essential. When the pH of the entire contents of the waste holding tank has been reduced to 2.0 and 3.0, a booster pump is started and sulfur dioxide is fed to the system until all the chromate has been reduced to trivalent chromium by test. When this has been accomplished the caustic pump is started and caustic fed continuously until the pH is in the range of 8.0 to 8.5. Again a pH recorder-controller may be used, however, a simple measurement of pH is adequate. When the pH of the entire contents of the waste holding tank has been elevated to the proper level, the circulating pump is shut off and the contents of the tank allowed to settle for 1 to 2 hours. Precipitated chromium hydroxide will settle into the conical bottom of the waste holding tank. Following the settling period, the drain valve on the holding tank may be cracked open an the sludge drawn off to a sludge pit or other suitable means for its removal by haul away or disposal in sludge drying beds. After the settled sludge has been removed from the waste holding tank, the chromium free liquid may be drawn off to waste. The holding tank is again ready for refill.

The batch destruction system will normally require more operator attention than a continuous system but will insure that only completely treated wastes will be discharged.

Continuous destruction systems will be applicable when the blowdown rate exceeds 25 to 30 gpm on a continuous basis, eliminating the need for a large holding tank and minimizing labor requirements.

CONTINUOUS SYSTEM

The treatment of chromate bearing cooling tower blowdown water on a continuous basis is illustrated in Figure 2. Sulfuric acid is pumped into the constant rate blowdown stream to depress the pH to 2.0 - 3.0. Next, sulfur dioxide effect of SO_2 on pH is added to reduce the chromate to trivalent chromium in the reaction tank and finally a lime slurry is fed to the waste stream in a small mixing tank to precipitate the chromium hydroxide. By elevating the pH to a range of 8.0 - 8.5, the precipitated chromium hydroxide is allowed to settle out in the 2 hour settling basin equipped with a sloped bottom to facilitate sludge concentration and removal. Periodically the sludge drain valve must be opened and the accumulated sludge run off for removal to sludge pits, drying beds, or hauled away.

In some cases with smaller installations, the lime slurry feeder may be replaced by a caustic feeder for the convenience of handling and operating. In place of sulfur dioxide the user may prefer sodium sulfite, bisulfite, metabisulfite or ferrous sulfate.

With a chromate bearing waste stream of relatively constant composition such as one would expect with the blowdown from a cooling tower, automatic pH controllers or chemical feeders may not be required. Once the chemical feeds are set, they should require little attention except to recharge them with chemical.

As the volumetric rates of blowdown discharge increase, the gravity settler with a sloped bottom for sludge concentration becomes prohibitively expensive and would be replaced by a clarifier equipped with a sludge scraper. This will insure adequate removal of sludge from the settling basin as well as maintain the sludge concentration as high as possible. Figure 2B illustrates the substitution of the clarifier with sludge scraper arms for the gravity settling basin. The gravity settling basin with the sloped bottom becomes impractical at flow rates much in excess of 100 to 125 gpm.

DEPTH FILTRATION

Recently a more economical approach to the removal of precipitated chromium hydroxide has become available. This is known as 'depth filtration' and utilizes a multilayer, granular type filter in conjunction with a coagulant aid feeder. Figure 2C shows the chromate reduction and precipitation steps as described before. However, the wastewater carrying the chromium hydroxide may be admixed with a small amount of polyelectrolyte type coagulant aid and pumped through the depth filter. The suspended solids are removed by the multilayer filter bed and chromium-free water produced. Because of the pretreatment with the coagulant aid and the multilayer media, this filter is capable of treating several times the volume of water obtainable with straight sand or anthracite filtration and at increase throughput rates. Such a system becomes attractive in higher flow plants where the gravity settler becomes prohibitive in size and the clarifier expensive.

The filter must, of course, be cleaned by backwashing and the resulting sludge disposed of by haul away from a sludge pit or other sludge holding vessels. Approximately 1 - 2% of the volume of waste filtered will contain the sludge in concentrated form.

The coagulant aid normally fed at a dosage of 0.5 - 1.0 ppm which adds between 5 and 10¢ per pound to the cost of treating and removing chromate.

The filtration system has the advantage of being compact in size and can be designed for automatic operation with backwash frequency established on a programmed basis.

ION EXCHANGE METHOD

Within the last several years an ion exchange technique has been developed specifically for the removal of chromate from cooling tower blowdown. This system utilizes an anion exchange column operating on the chloride cycle to selectively extract the chromate ion from the other ions in solution.

In operation, the pH of the blowdown stream is adjusted to 4.5 - 5.0 by direct acid injection. At the normal chromate levels in cooling tower blowdown water (15 to 20 ppm), the unit has the capacity to operate 3 - 4 days between regenerations when treating a feed free of suspended solids.

Regeneration is carried out by a sodium hydroxide - sodium chloride solution which strips the absorbed chromate from the ion exchange bed in a 1 - 2% concentrated solution which may be sent to a holding tank. There are two alternatives in the handling of the eluted chromate solution:

1. Reuse
2. Destruction of chromate

REUSE

Since the recovered chromate solution contains none of the other inhibitor components such as zinc or phosphate, it must be fortified with a treatme[illegible] which is essentially free of chromate but rich in the non-chromate constituents.

In addition, since the chromate recovery system does not recover the chromate lost with windage or carryover, a 'balanced' inhibitor might be required to supply this makeup. On the basis of reuse of chromate recovered from the blowdown only, a chemical operating cost of about 5¢ per pound CrO_4 recovered is expected.

Equipment costs will be related to the flow rate which must be handled. In addition, the ion exchange system is sensitive to the presence of suspended solids, oil, plankton, algae, etc. which are normally found in cooling tower blowdown waters.

If these elements are present, the tower blowdown will require filtration prior to the ion exchange unit. Where cooling towers have side stream filters in service, the ion exchange chromate recovery system should be installed to treat the clean filter effluent. If no side stream filters are installed, a separate prefilter before the chromate recovery unit may be necessary.

Table II summarizes the ion exchange chromate recovery system sizing, capacity and estimated selling price. At least one water treatment equipment manufacturer is presently offering these recovery units as skid-mounted, preassembled, automatic systems. Pricing data in Table II reflects this basis both with and without prefiltration.

DESTRUCTION OF CHROMATE

In the event that the reuse of the chromate presents more of a problem than its value such as would be the case with a small system, the eluted chromate can be destroyed chemically in a batch destruction tank by the methods described above. In this case, the ion exchange system serves as a concentrating device reducing a high volume - low chromate content stream to a low volume, chromate-ri stream (regenerant) which can be easily handled in a small batch destruction tank. Several systems are operating at present in this fashion.

The ion exchange system for handling chromate bearing cooling tower blowdown water is shown in Figure 3. In this case, no reduction or precipitation of chromate is effected. The chromate contained in the blowdown water is removed from solution by the ion exchange unit and the chromate free effluent directed to the sewer or water course.

On regeneration, sodium chromate is eluted and collected in a holding tank. As previously indicated, the chromate may be batch destroyed in the conventional fashion or fortified for reuse as part of the cooling system inhibitor program.

The ion exchange chromate recovery system can be readily automated to minimize the need for operator attention.

APPLICABILITY OF REMOVAL TECHNIQUES

In choosing from among the several systems described in this report, one must be guided by the volumetric rate to be treated, the quality of treatment necessary and the user's local conditions. In order to provide the reader with an appreciation of the applicability of each of the methods described to the solution of a specific waste problem, Figure 4 plots the estimated equipment cost for the batch destruction system, continuous destruction systems, and ion exchange method of removing chromate from cooling tower discharge. The estimates of capital equipment investments and chemical costs, which are tabulated on Table I will provide the user with a first approximation of the cost for chromate removal.

CONCLUSIONS

It has been the intent of this report to provide the reader with a survey of the several methods and techniques available for the removal of chromate from cooling tower blowdown water. Because of the great diversity of State and local pollution codes, no firm statement can or should be made regarding a universally applicable technique. In any but the smallest system, the reader is cautioned to investigate and treat each case individually. No judgment should be made as to the appropriate system or treatment to be effected without a full appreciation of the unique conditions relating to the particular installation being considered.

LS/cam
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BETZ LABORATORIES, INC.

CrO_4

$Na_2SO_3 = 45 \frac{\#}{10^6 \# water} \left(\frac{10^6 \# water}{20 \# CrO_4^=} \right) = 2.25 \frac{\# Na_2SO_3}{\# CrO_4^=}$ reac

Values based on Theoretical amou[nt] required for conve[rsion] of $CrO_4^=$ to $Cr(OH)_3$ MUST ADD amount for dissolved oxyg[en]

@ 130°F O_2 = 4 cc/liter

#/10^6# water
45

Na_2SO_3 200 $Fe(SO_4)$

TABLE I

CHEMICAL REQUIREMENTS CHROMATE REMOVAL THEORETICAL VALUES FOR 1# CrO_4

	Reducing Agent				
	Sulfur Dioxide	Sodium Bisulfite	Sodium Sulfite	Sodium Metabisulfite	Ferrous Sulfate · $7H_2O$
# Reducing Agent	1.11	1.81	2.19	1.66	9.65
for O_2 reaction	1.1		2.50		10.00
# Acid (H_2SO_4)	0	0.86	1.71	0.86	3.41
# Alkali ($Ca(OH)_2$)	1.29	1.29	1.29	1.29	2.58
Price Reducing Agent ¢/lb	11.0	5.3	4.3	5.4	1.72
Cost Reducing Agent ¢/lb CrO_4	12.3	9.6	8.8	8.9	16.6
Cost for O_2 Removal	12.1		10.7		17.2
Cost Acid ¢/lb CrO_4	0	1.3	2.55	1.3	5.1
Cost Alkali ¢/lb CrO_4	0.7	0.7	0.7	0.7	1.3
Total Theor. Chem. Cost ¢/lb CrO_4	13.0	11.6	12.1	10.9	23.0
With O_2 removal	25.1		22.8		27.2

NOTE: When using SO_2 as reducing agent, actual requirements may be 3 - 4 times stoichiometric, therefore H_2SO_4 is normally used to depress the pH to 2 - 3 before SO_2 is applied.

Chem. Costs

TABLE II

IX CHROMATE REMOVAL SYSTEM

Dia. Unit Inches	Capacity GPM	Capacity M Gals at 20 ppm CrO_4	CrO_4 Capacity #/Cycle	Selling Price $ No Filter	Selling Price $ With Filter
12	12	75	12.5	5000	6500
18	25	170	28.5	5500	7250
24	50	240	40.0	6450	8700
30	60	374	62.5	7900	10750
36	115	560	93.5	9700	13500
48	200	960	160	12000	17750
60	315	1500	250	16000	24500

700 gpm ——— $50,000

Contineous ——— $100,000

NOTE;

1. Regeneration Requirements - 2# NaCl/#CrO_4
   0.5#NaOH/#CrO_4
   0.5#H_2SO_4/#CrO_4

2. Pricing based on skid-mounted, preassemblea, automatic system but exclusive of holding tank or treatment for recovered CrO_4. Filter included - pressure type, automatic.

Title - Ion Exchange System
Chromate Removal
Cooling Tower Blowdown

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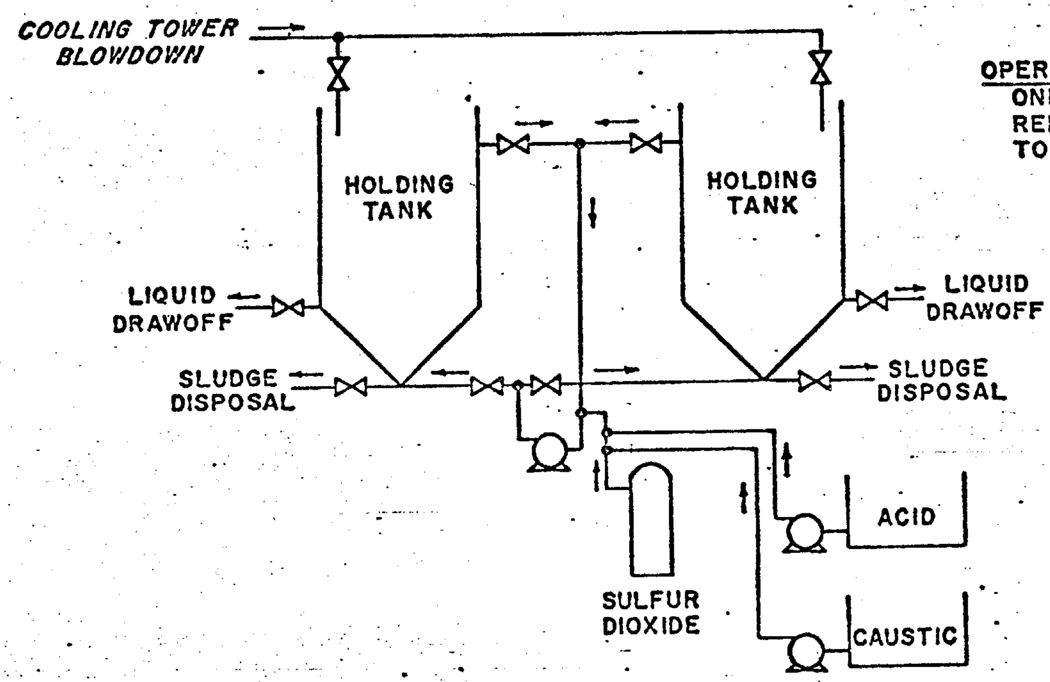
CHROMATE REMOVAL SYSTEM



OPERATION:
ONE BATCH HOLDING TANK IS BEING REFILLED WHILE THE OTHER IS USED TO TREAT FOR C_rO_4

NOTES:
(1) ALL PIPING, VESSELS, AND PUMPS MUST BE BOTH ACID AND ALKALI RESISTANT.

Fig. I

BATCH PROCESS

CHROMATE REMOVAL SYSTEM

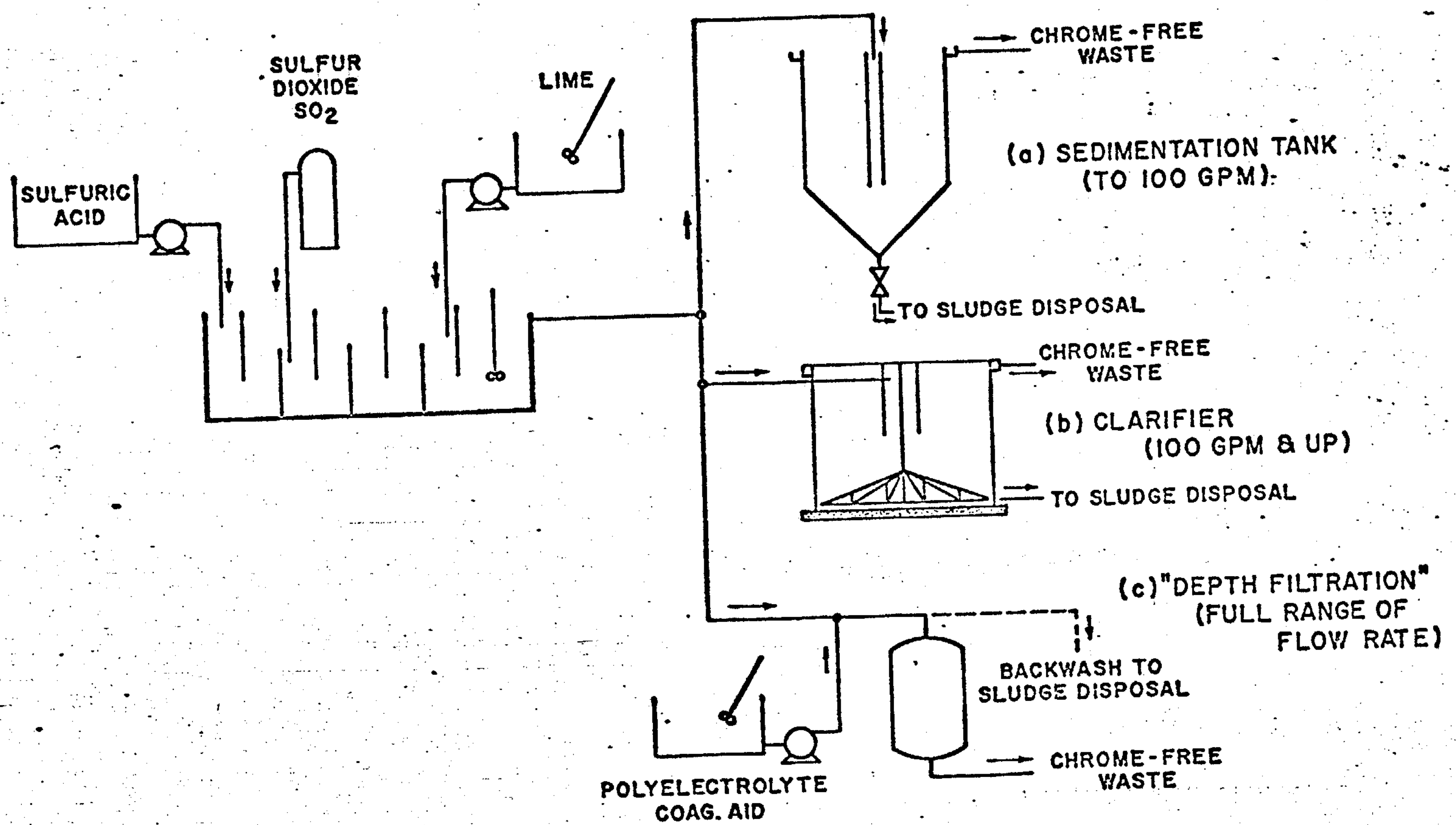


Fig. II

CONTINUOUS PROCESS

CHROMATE REMOVAL SYSTEM

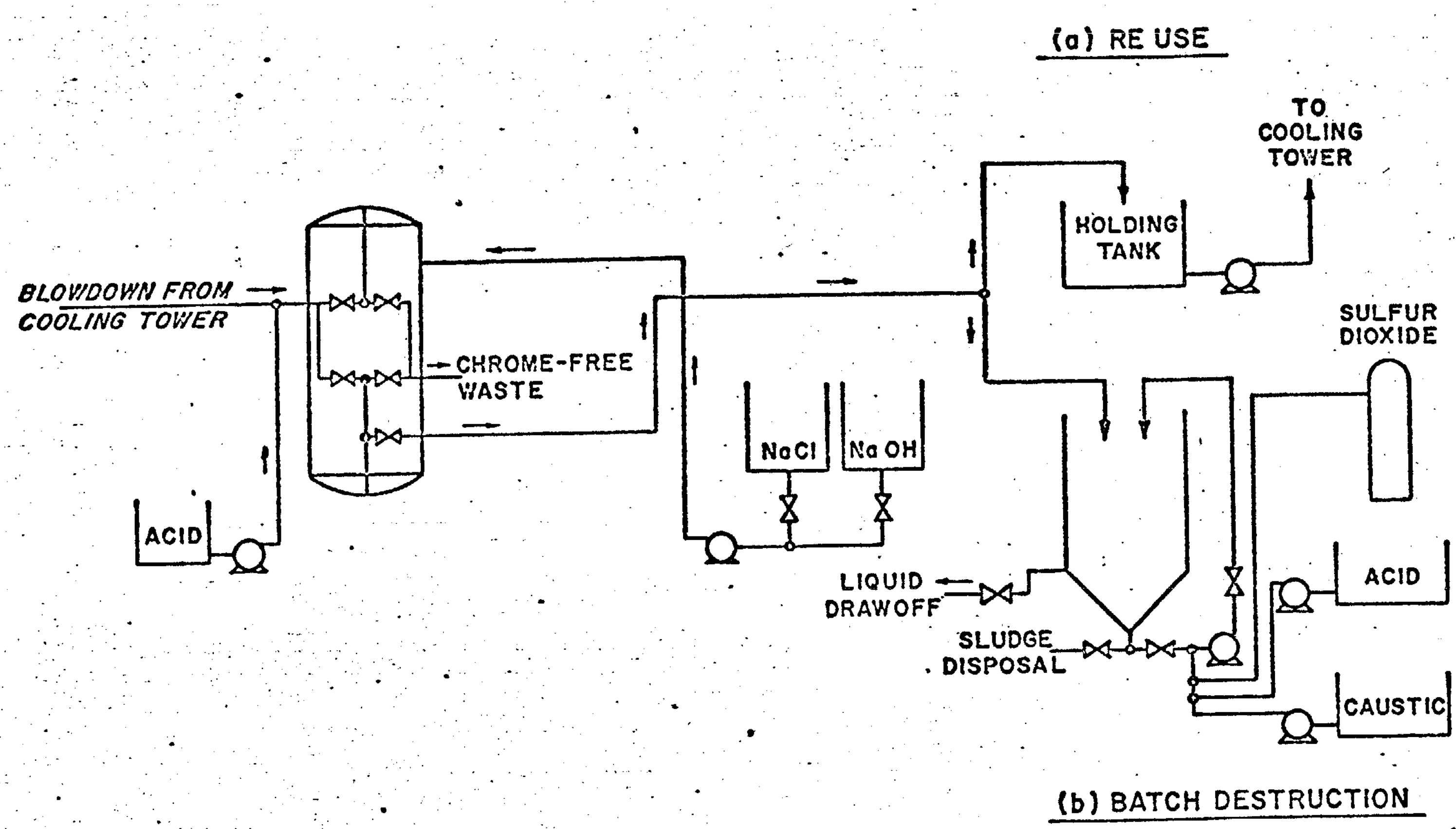


Fig. III

ION EXCHANGE PROCESS

CHROMATE REMOVAL SYSTEM

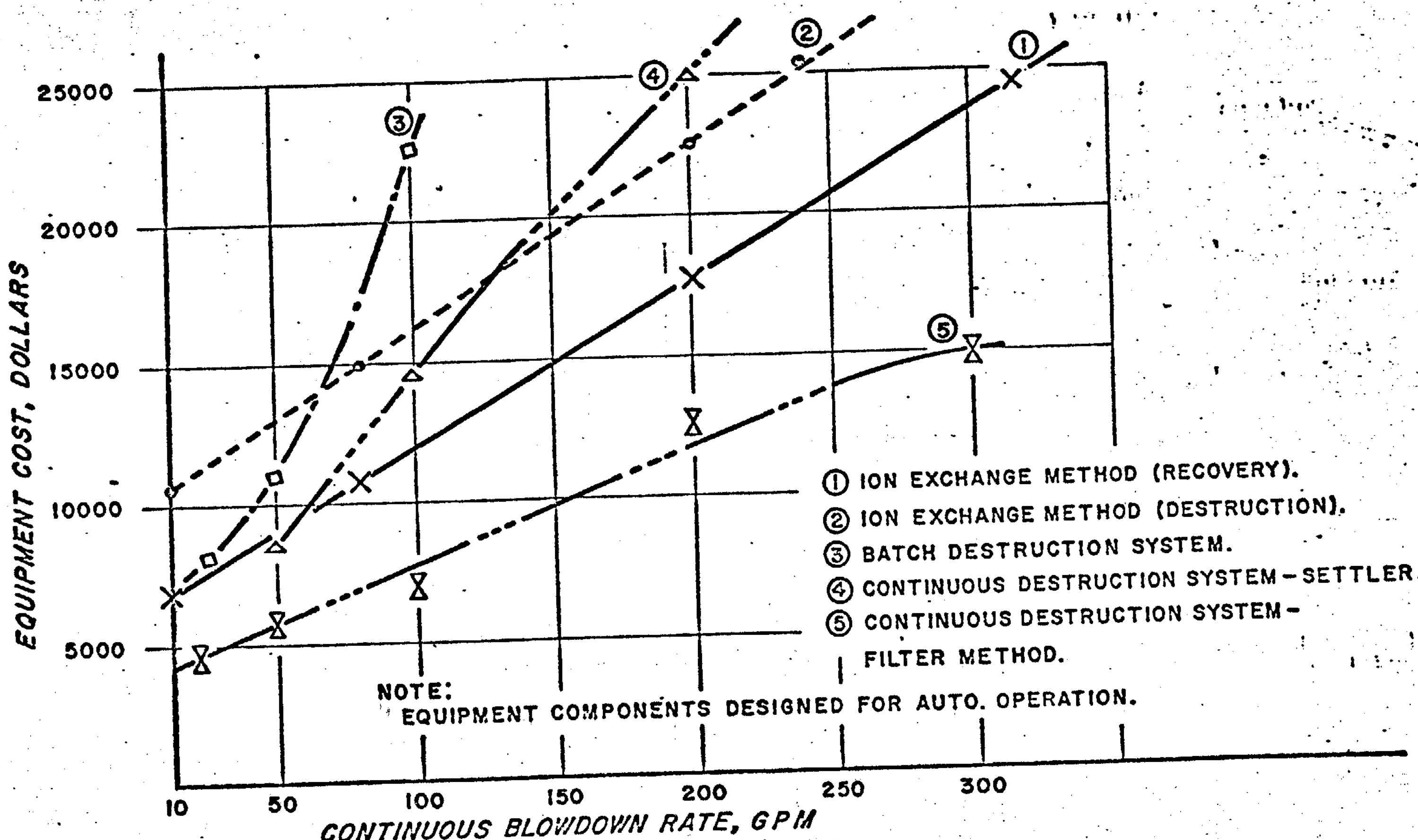


Fig. IV

COMPARATIVE COSTS FOR EQUIPMENT

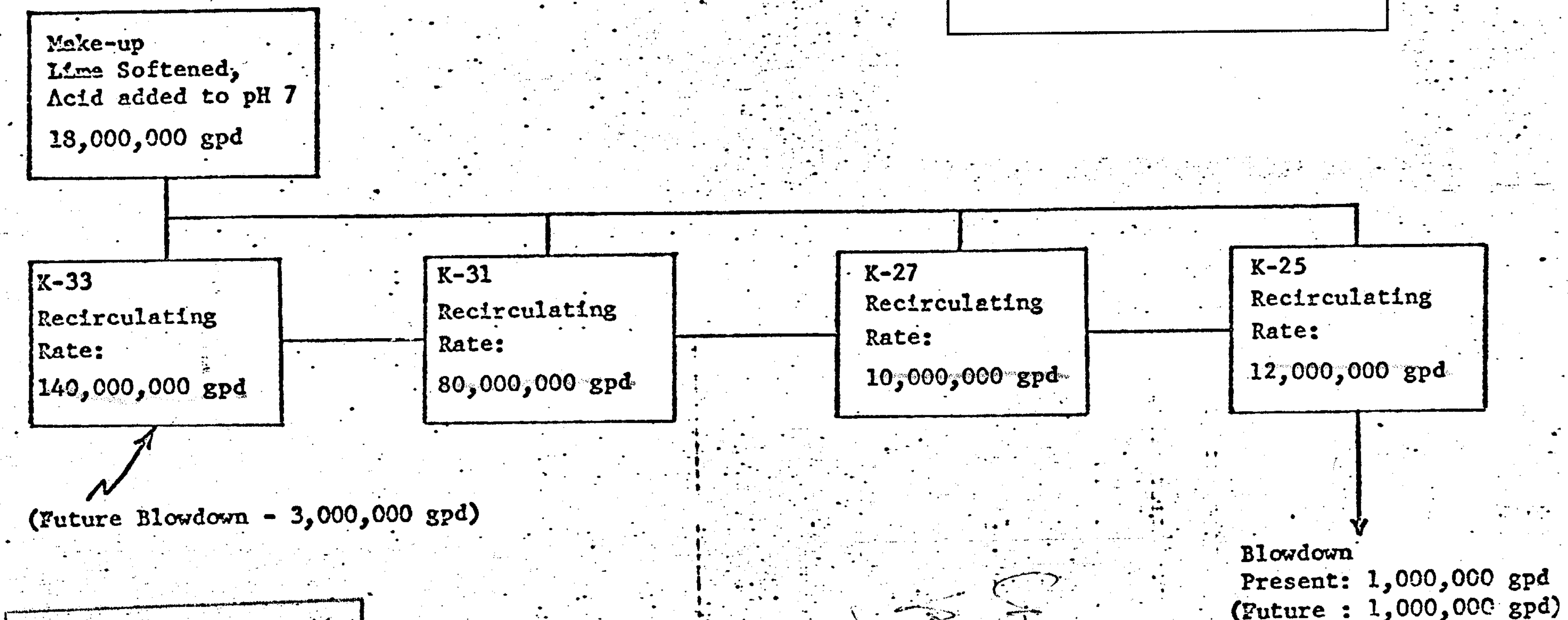
Chromate Recovery

Chromate salts are added to the recirculating cooling water (RCW) to retard corrosion of the copper tubes in the heat exchangers, but a portion of this water, after 3 to 12 cycles through plant heat exchange equipment, must be discharged to the Scioto River to prevent the dissolved solids from exceeding a tolerable level. Since the chromate circulates through the system unchanged, this discharge or blow-down represents a loss of the costly chromate and adds to the pollution of the river.

Several years ago development work on the recovery of chromate from the blow-down water was begun; initial work was based on the use of anionic exchange resins. Laboratory scale experiments proved that, through proper pH control, resins of the type ordinarily used for water softening would remove most of the chromate from the RCW blow-down. The use of anionic exchange resins is now in the pilot plant phase. The following problems are of immediate concern: quantity of trivalent chromium formed in the column; the effects of the water on the stability and longevity of the resin; and the extent of leakage of the chromate ion into the blow-down water.

Concurrent with these pilot plant studies, laboratory studies of the fundamental aspects of chromate recovery by ion exchange are being made. Tests run with RCW at a pH of 3.5 and the resin column at a pH of 6.5 showed little or no formation of trivalent chromium. However, a leakage of chromate ions into the blow-down stream does occur. When the resin column is adjusted to a pH of 3.5, the chromate leakage is greatly reduced, but some chromate is lost through reduction of the chromate ion to trivalent chromium. Laboratory work will continue towards optimizing the conditions for chromate recovery; the role played by organic materials present in the RCW in causing resin fouling and destruction also will be investigated.

Other methods of chromate recovery also are being explored: recovery in a foam created by a cationic surfactant; adsorption on activated alumina; and electrolysis through a permeable membrane. In a laboratory experiment, 75 per cent of the chromate in the RCW was recovered in a foam created by adding 150 ppm of lauryl pyridium chloride (a cationic surfactant) to the water and blowing air through the solution. The chromate ion has also been recovered by passing the RCW through a column of activated alumina, but quantitative results are not yet available. Commercially, it is feasible to convert brackish water into potable water by electrolysis through a permeable membrane; therefore a literature search is being made to determine whether this method is applicable to recovery of chromate from the RCW.



Calgon part of proposal they seem to push Ferrous metal treatment ?

Union Carbide Corporation Nuclear Division Oak Ridge, Tennessee	HALL LABORATORIES DIVISION OF CALGON CORPORATION PITTSBURGH, PENNSYLVANIA	PRINTED IN U.S.A. DR. KK DATE 8/17/66 SCALE None
		Exhibit I

1617
Y/HG-0548

Y-12

A. Implementation of 1971 Recommendations

No recommendations were made during the 1971 appraisal.

B. Recommendations of the 1972 Appraisal

1. Evaluate alternate methods of meeting Tennessee air pollution emission limits from the steam plant. Assume that dependable flue gas cleanup systems will remain to be technologically infeasible for small, Y-12 size steam plants through early 1975 when a firm plan of action should be underway to meet the July 1, 1977, deadline.

2. Implement a plan by June 30, 1973, which will reasonably assure meeting the dissolved oxygen minimum limit of 5 ppm in East Fork Poplar Creek at the outfall of New Hope Pond.

3. Expand the investigative measures to the level necessary to promptly identify the sources of hexavalent chromium responsible for exceeding the fish and aquatic life limit of 0.05 ppm in East Fork Poplar Creek. The Y-12 data indicate that this concentration has been exceeded over 70% of the months in the past few years since this contaminant has been identified as a problem.

4. Identify and correct the sources of "slug" discharges of acids and bases into East Fork Poplar Creek which are responsible for exceeding the Tennessee limit of more than one pH unit change in 24 hours. In addition, the pH fluctuation data should be routinely included in the Air & Water Manual to give a more accurate picture of Y-12's compliance posture and to aid in alerting selected plant supervision to potential problems.

5. Cease disposing of waste oil in the burial ground "rat holes." Instead, utilize controlled surface disposal, probably in the burial ground, with Development Department coordination. Experimental surface disposal and associated biodegradation shows great promise. Although these experiments are not complete, they should be pursued aggressively and a larger scale field test appears to be desirable.

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